THE CHEMISTRY

OF

INDIA RUBBER,

INCLUDING THE OUTLINES OF A THEORY ON VULCANISATION.

BY

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With Four Plates and Several Illustrations in the Text.

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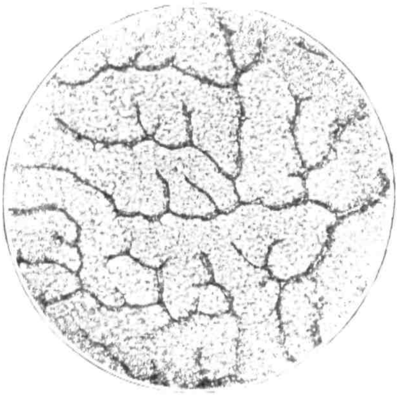

FIG. 1.—Structure of Insoluble Constituent of India Rubber.
Photo-micrograph: Apochrom. Zeiss 8 mm., Projec. Eyep. 4. × 210.

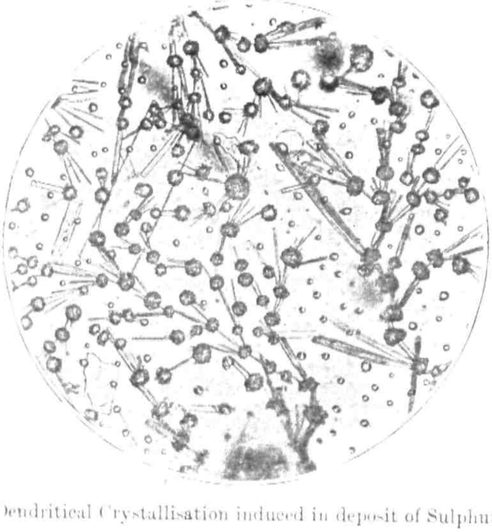

FIG. 15.—Dendritical Crystallisation induced in deposit of Sulphur Globules.
Photo-micrograph: Apochrom. Zeiss 4 mm., Projec. Eyep. 4. × 600.

Dedicated

TO THE

MEMORY OF DR. ROBERT HENRIQUES,

IN HIGH APPRECIATION OF HIS WORK

ON THE ANALYSIS

OF

INDIA RUBBER.

PREFACE.

In undertaking, at the request of the publishers, to write this book, the chief inducement to me was the hope of arousing the interest of chemists and technologists alike in the study of the scientific aspects and problems of the remarkable class of substances known as india rubber, the very name of which would seem to suggest that our present day knowledge of them consisted chiefly in the fact that they may be used for erasing pencil marks.

The intention in the first instance was to deal, in the following pages, simply with the analytical methods, which are almost exclusively the work of R. Henriques, more particularly as regards the rubber substitutes so-called, and my own researches, chiefly concerning india rubber itself and the vulcanisation problem. This refers to work done within the last ten years. Before that time india rubber analysis, if it existed at all, was unknown to the outside world. But I discovered very soon that a mere compilation of analytical methods could at best only claim a very limited technical interest, and only point the way to obtaining a number of statistical data respecting india rubber and its manufactures, without affording any solid basis for their subsequent interpretation. This might have sufficed for those who simply want to 'do' india rubber, but would have rendered the work almost worthless to those who hereafter may feel inclined to turn their attention to a field of inquiry equally fascinating in its chemical, physical, physiological, and technical aspects. I resolved, therefore, to enlarge the scope of the work by the introduction of a chapter on the "Chemistry of India Rubber." The literature on this subject is extraordinarily scanty, and at the same time, with perhaps two or three exceptions only, untrustworthy to a degree. The writing of this chapter proved, therefore, a very arduous task, and involved an amount of work altogether out of proportion to its volume.

Incidentally I felt compelled to deal at some length with the nature of the colloidal state itself, the phenomena of which have an important bearing upon the chemical, and still more upon the technical, behaviour of india rubber. Indeed, the fact that india rubber is a colloid may be said to constitute the root difficulty of this subject to the chemical investigator and the technologist alike. All these circumstances together led to the book assuming the form of a monograph rather than of a text-book.

Of the many unavoidable gaps, of the many points I had to leave undecided or only half discussed, I am only too painfully aware, and in excuse can only plead the limitations of one largely engaged in technical work. Some of these omissions I hope to supply in the future; many, I trust, will be made good by the work of others.

Manufacturing processes as such have not been dealt with, as to have done so would have resulted in the destruction of the unity and aim of the work; but I shall not be surprised to meet with the criticism from certain quarters that, as a consequence of this restraint, the book is too theoretical. I am content to let it be so.

The cradle of the india rubber industry, as of so many others, stands in this country, which, from her former paramount position in almost every one of them, has fallen, and is still falling, to the second or third place, or no place at all—a result owing in large part to the shortsightedness of the manufacturers who conduct their undertakings simply on what they are pleased to call 'practical lines,' which so often means that all forethought and present research is sacrificed to the reaping of immediate profits, the future being left to take care of itself entirely. The rude awakening which the national industries are experiencing at the present moment has—perhaps naturally enough considering the state of mind of their leaders—resulted in a gross misconception of the nature of the industrial stimulus operating abroad, precipitating the country into a feverish craze for stuffing the heads of ignorant schoolboys with 'technical education.'

Salvation is to be found in the 'technical education' of the working classes, but that the 'masters' stand infinitely more in need of education than any other class of the community has scarcely been realised yet. Until the nation, as a whole, recognises that the prosecution of scientific study as a mere means of money-making is a profanation defeating its own ends, the history of industrial development in England will afford the same melancholy spectacle in this as in the last century, so-called technical education notwithstanding.

As regards the india rubber industry, it is still very largely developing

on empirical lines. In none of the industrial countries have any organised efforts been made to bring to bear upon the problems of this industry the full resources of modern chemical and physical research. This is, no doubt, also the reason why, notwithstanding the occasional claims of 'trading puffs,' the efficiency of the rubber trade in Great Britain is in no way inferior to that of either the United States, Germany, or France. But it is of importance that manufacturers should clearly realise that india rubber, and the industry connected with it, offer wide fields for scientific research, the exploration of which has already commenced; and the india rubber industry of the future will belong to whatever country may take the lead in the scientific investigation and elaboration of its problems. The coal tar colour industry has been lost to Great Britain through the indifference of her statesmen, the shortsightedness of her manufacturers: is her india rubber industry to suffer the same destiny?

At the end of the book will be found a short chapter on the "Sanitary Conditions in India Rubber Works," a matter of not inconsiderable importance with which the chemist is much more competent to deal than the engineer.

To my former assistant Dr. F. Betteridge I am indebted for help in connection with some of the researches contained in this book, and to my son Mr. L. E. Weber for the preparation of the micro-slides and photo-micrographs which illustrate certain sections.

THE AUTHOR.

CRUMPSALL, *November* 1, 1902.

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INDIA RUBBER AND ITS ANALYSIS.

CHAPTER I.

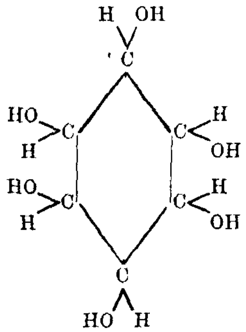
THE CHEMISTRY OF INDIA RUBBER.

No class of bodies offers such formidable manipulative difficulties to the investigating chemist as the remarkable group of colloids comprised under the collective name of india rubber. These difficulties are physical rather than chemical—that is to say, they do not so much consist in the functional complexity of the molecules of india rubber, as in the circumstance that these molecules are, at any rate at present, known only with the colloidal state superimposed upon them. Matter in this state does not exhibit the abrupt changes of physical condition which, in crystalloids, take the form of melting points, boiling points, and solution. The physical changes induced in colloids by heat, or by solvents, are perfectly continuous changes as long as the underlying chemical molecule or configuration remains intact. As a consequence, the characterisation and identification of the colloids and their derivatives, and their isolation and purification from mixtures of them, offers frequently almost insuperable difficulties.

India rubber, as is well known, is the product of the coagulation of the milky juices (emulsions) of a large number of trees, creepers, and shrubs, comparable in this respect to the oils, and more particularly to the terpenes. Accordingly, the commercial article can hardly be expected to be a homogeneous, and still less a pure, product in the chemical sense. Indeed, a cursory examination of a few samples at once reveals the presence in them of water, sand, vegetable fragments, fibres, wood, and other more or less accidental impurities. These may be removed by a washing process, which, however, can only be satisfactorily carried out on a commercial scale, strong machines being needed for the purpose. The water also removes from the india rubber certain carbohydrates (sugars), the presence of which in various brands was discovered by Aimé Girard,[1] together with practically the whole of the above named mechanical im-

The carbohydrates thus removed are :—*inosite*, *bornesite*, *matezite*, and *dambonite*.

Inosite occurs in Gaboon rubber; it is identical with Girard's dambose (MAQUENNE).[1] According to its constitution, it is one of the numerous stereo-isomeric hexa-oxy-hexa-methylenes :—



$= C_6H_{12}O_6$.

The inosite of Gaboon rubber is i-inosite (inactive). It is soluble in water, alcohol, and acetic acid, and crystallises in fine needles (M.P. 225° C., B.P. (in vacuo) 319° C.).

Bornesite, *mono-methyl-a-inosite* $C_6H_{11}O_6.CH_3$, occurs in Borneo rubber. It crystallises in white rhombic prisms, readily soluble in water, little soluble in alcohol. Its melting point lies at from 199° to 203° C.; at 205° C. it sublimes almost without decomposition. It is optically active, dextro-rotary ($a_D = +31 \cdot 6°$).

Matezite, which occurs in Madagascar rubber, is the mono-methyl ether of i-inosite. M.P. 186° C.; sublimes without decomposition at 200° C. Very soluble in water, sparingly soluble in strong alcohol, insoluble in absolute alcohol. It is dextro-rotary ($a_D = 65 \cdot 7°$).

Dambonite occurs in Gaboon rubber, and is the di-methyl ether of i-inosite $C_6H_{10}O_6(CH_3)_2$. It crystallises, with three molecules of water, in the form of white hexagonal prisms readily soluble in water and alcohol. M.P. 195° C.; sublimes without decomposition at 210° C. Dambonite is optically inactive.

These sugars seem never to be present in any larger quantity than 0·5 per cent., but the average percentage is rather lower. They are, of course, completely removed from the rubber by the washing operation above referred to.

The drying of the washed rubber is best performed in vacuo, to prevent the otherwise unavoidable oxidation. The substance then forms technically pure rubber, but is by no means chemically pure, as solvents, such as alcohol or acetone, readily extract from it certain oily and resinous matters. The amount of these in the different brands of india rubber varies enormously, from 1 to about 40 per cent. Nor is the quantity

constant in the same brand, the less so the greater the average amount of resinous matter usual in any given brand. Thus, while the amount of such matters in Pará rubber varies from 1 to 2 per cent., it varies in Lagos rubber from 3·6 to 7 per cent., and in Borneo rubber from 6 to 21 per cent. The removal of these resinous and oily matters from the india rubber is readily effected by extracting a weighed quantity of the india rubber with acetone in a Soxhlet extractor. For this purpose it is, however, essential to use the rubber in the form of the highly porous washed sheets as they are obtained in rubber factories. If cut pieces of crude rubber are used, the complete extraction becomes an extremely tedious operation. The following tables show the percentages of extract obtained from various brands of india rubber :—

Brand of India Rubber.	Percentage of Resinous Extract.		
	Terry.[1]	Weber.[2]	Henriques.[3]
Pará, fine,	1·2 per cent.	1·3 per cent.	1·3 per cent.
Ceara Scraps,	1·3 ,,	2·1 ,,	2·1 ,,
Columbia,	2·5 ,,	3·8 ,,	5·0 ,,
Mozambique,	3·0 ,,	3·2 ,,	3·8 ,,
Manoh Twist,	...	2·9 ,,	5·8 ,,
Lagos,	...	4·4 ,,	4·5 ,,
Rio Janeiro,	5·8 ,,	5·2 ,,	2·5 ,,
Madagascar,	6·4 ,,	8·2 ,,	7·1 ,,
Sierra Leone, red,	7·4 ,,	9·7 ,,	5·8 ,,
Borneo,	7·9 ,,	11·7 ,,	10·0 ,,
Assam,	9·3 ,,	11·3 ,,	11·3 ,,
Mangabeira,	10·5 ,,	13·1 ,,	5·8 ,,
African Ball, I.,	18·5 ,,	22·8 ,,	...
,, II.,	22·8 ,,	26·1 ,,	...
African Flake,	41·2 ,,	63·9 ,,	...
Balata,	...	8·4 ,,	...
Gutta Percha (Penang),	...	9·3 ,,	...

How far these figures are correct depends, of course, upon the efficiency of the solvent employed—*i.e.*, its ability to dissolve all such resinous bodies as may occur in india rubber. As regards this point, it is worth while to draw attention to the fact that, of the large class of resins proper, the great majority are either insoluble, or only partially soluble in acetone, so that the acetone might leave undissolved certain resinous bodies occurring in india rubber.

Indeed, in Sierra Leone rubber, both red and white, I have ascertained the presence of a considerable quantity of a resin, in its appearance closely resembling crude albane as obtained from gutta percha, which is only very sparingly soluble in even boiling acetone. The complete extraction of this resin from the rubber requires days, and it is not impossible that

other brands of rubber may contain similar resins, so that the above figures might be open to very considerable correction.

No such relations as obviously exist between gutta percha and the resins invariably accompanying it have been shown to exist between india rubber and its native resinous impurities.

The nature of the resins extracted from various brands of india rubber varies very greatly. In some cases a distinctly oily extract is obtained, in others treacly masses, in others resins similar in appearance to colophony, or elemi resin, and in a few cases white powdery products, in appearance resembling the crude albane of gutta percha, but in every case differing from it in composition. Respecting the chemical character of these extracts nothing at all is known.

These resinous impurities determine to a considerable degree the behaviour, especially of the inferior brands, of india rubber in practical working, and they are also supposed to have a marked influence upon the stability of the finished article. The technical effect due to the presence of these resins must, no doubt, be ascribed to their decided action upon the sulphur in the vulcanising process; but seeing that the presence of these resins in crude india rubber does not appear to affect its stability in an appreciable degree, it is difficult to understand why they should act detrimentally after vulcanisation—a process which is generally admitted, and rightly so, to enhance its chemical indifference. The explanation of this mistaken supposition lies probably in this, that undervulcanised india rubber, or india rubber vulcanised with an insufficient amount of sulphur, is well known to be highly perishable. Now, it is evident that in vulcanising india rubber either without taking into account the amount of resin present, or underrating that amount, more or less of the sulphur intended for the vulcanisation of the india rubber is taken up by the resin. The result is an undervulcanised, and therefore unstable, vulcanisation product. Such a product may still contain free sulphur, but not sufficient to induce vulcanisation at the temperature employed. This, of course, might be rectified by increasing the temperature of vulcanisation, but such increase of temperature would equally favour the combination of the residual sulphur with the resin, so that the final result would remain essentially unaffected.

A thorough study of these 'resins' will very likely enable us in the future to determine in manufactured goods the chief kinds of india rubber employed. At the present time this is impossible, although it is quite within our power to determine whether a given article has been manufactured from a high, medium, or low grade rubber.

It is only to be expected that crude rubber, besides the above named carbohydrates, should also contain albuminous matters (proteids) which invariably form one of the constituents of the latex of the india rubber

at least at present, employed in the preparation of the different brands of india rubber. If BIFFEN'S[1] centrifugal method were generally adopted, this impurity would be almost completely avoided.

The percentage of these proteïds in the rubber is small, but, as to its exact amount, we possess no reliable data. SEELIGMANN[2] quotes the composition of the latex as:—

India rubber,	32
Proteïd and mineral matter,	12
Water,	50

These data are altogether too vague. FARADAY gives the following analysis of the latex of *Hevea braziliensis*:—

India rubber,	37·70 per cent.
Albumen,	1·90 ,,
Bitter nitrogenous substance soluble in water and alcohol,	7·13 ,,
Substance soluble in water, insoluble in alcohol,	2·90 ,,
Wax,	0·13 ,,
Water, slightly acid,	50·37 ,,

From these figures it would follow that Pará rubber would contain about 4·3 per cent. of albuminous matter, but I consider the presence of such an amount highly questionable, although LASCELLES-SCOTT[3] states it even higher than this in a latex of unnamed origin:—

India rubber,	37·13 per cent.
Albumen,	2·71 ,,
Resins,	3·44 ,,
Essential oils,	Traces.
Sugar,	4·17 ,,
Mineral matter,	0·23 ,,
Water,	52·32 ,,

According to these figures the percentage of proteïds in the dry rubber would amount to about 5·6 per cent. The absence of information respecting the origin of the above milk is to be regretted, as its very high percentage of sugar and its quite unusually low percentage of mineral matter alike render it very remarkable.

On the large scale the removal of these proteïds from the commercial india rubber is a practical impossibility. On the small scale they can be eliminated by dissolving the india rubber and allowing the dilute solution to stand, when the insoluble coagulated proteïds gradually settle out. A somewhat more expeditious method is the centrifuging of the solutions. From these solutions the india rubber is precipitated by alcohol, and the product thus obtained, when dry, appears to have always been looked upon as chemically pure india rubber. At any rate, all known analyses of india rubber, with the exception of those made by GLADSTONE and

HIBBERT,[1] have been made with products freed from the various impurities named above. The last named were the first to clearly recognise the presence of comparatively small and varying proportions of oxygen in india rubber, and they also observed that by fractional precipitation the percentage of oxygen can be greatly reduced, although its complete elimination was found impossible.

The elementary composition of india rubber as determined by the earlier workers up to 1888 has been compiled in the following tables:—

	Faraday.	Ure.	Williams.	Berzelius.	Adriani.	Gladstone and Hibbert.	Calculated for $C_{10}H_{16}$.
Hydrogen,	12·8	10·0	12·1	12·5	11·94	12·00	11·76
Carbon, . .	87·2	90·0	87·3	87·5	87·91	87·46	88·24

It will be seen that these data agree fairly well with the figures calculated for a compound of the terpene type $C_{10}H_{16}$, and this formula is now generally held to express the quantitative composition of india rubber, although, in view of the impossibility of producing an absolutely oxygen-free product, HENRIQUES within recent years pointed out the possibility that india rubber might after all be found to be an oxygen compound.

PAYEN was the first to observe that on dissolving india rubber the greater part of it passed into solution, but that there remained always an insoluble constituent, consisting of very voluminous and gelatinous flakes, which, under the microscope, presented a peculiar reticulated appearance. For some extraordinary reason these two constituents appear never to have been analysed separately. By common consent the insoluble constituent was looked upon as an 'insoluble modification' of india rubber. GLADSTONE and HIBBERT[2] express themselves on this point as follows:—

"We are inclined to believe that the less soluble modification of the hydrocarbon which has been frequently observed is produced during the drying of the juice, for we find that if the more soluble part be heated, it is more or less changed, and less susceptible of subsequent solution. The change increases as the temperature is raised, and also with the length of time during which the heat continues. This will account for the very varied results obtained by different experimenters as to the proportions of soluble and insoluble caoutchouc."

Even more definite are SEELIGMANN'S[3] statements respecting the nature and relationship of these two constituents:—

"Le caoutchouc est, en effet, formé de deux substances isomériques, dont l'une, solide et élastique, résiste à presque tous les agents; tandis

que l'autre, demi liquide et poisseuse, est beaucoup plus facilement attaquée et dissoute. C'est à cette seconde matière que la gomme doit la propriété de se souder à elle-même lorsqu'on soumet à une forte compression ses surfaces récemment coupées. On donne à la première matière le nom de *nerveuse* et à la seconde le nom *d'adhésive*. Si, par une dissolution approprié, on sépare ces deux principes immédiats isomères, aucun d'eux ne garde les propriétés élastiques et extensibles au même degré ; il semblerait, dit Payen, que l'adhérence entre les filaments, lubrifiés par une matière grasse et assouplie par la portion soluble et molle, ait été partiellement détruite."

It will be observed that SEELIGMANN describes the two constituents in question as isomers, and that he, following PAYEN in this respect, ascribes to the insoluble constituent important physical functions. In this he appears to have been influenced by the statements of various authors, who found the percentage of the insoluble constituent or modification of india rubber to vary between 30 and 70 per cent., or an average of 50 per cent. GLADSTONE and HIBBERT, however, found only 4 per cent. of this insoluble body in Pará rubber.

In view of this very large and important discrepancy, I reinvestigated this subject.[1] The inner parts of a loaf of crude Pará[2] were split into very fine films. As these contain a considerable proportion of water, they were, to begin with, subjected to an often repeated treatment with acetone, during which they (originally cream-coloured films) assumed a pronounced tan colour. Finally, they were completely extracted with acetone in a Soxhlet extractor, and then, without drying, transferred into chloroform. After a little over a fortnight, during which time the bottle containing the solution was frequently shaken, a solution was obtained consisting of two layers. The lower of these was a bright clear solution, while the upper consisted of small clots or shreds of the insoluble part of the rubber. This upper layer, which appeared to represent a very substantial proportion of the rubber used, was removed, and a number of times treated with fresh quantities of chloroform, two or three days intervening between each of these changes of solvent. This treatment was continued until the chloroform extracted no longer any perceptible quantity of soluble matter from the flocculent jelly, the apparent bulk of which very greatly decreased during this treatment.[3] Finally, the product so purified was dried in

[1] *Journ. Soc. Chem. Ind.*, 1900.

[2] Washed rubber which has been sheeted in a 'rubber washer' cannot be used, as in this operation the flakes of the insoluble constituent are so broken up and comminuted, that the whole afterwards forms an apparently complete, homogeneous solution (rubber varnish).

[3] On a rough estimation this decrease amounts to quite five-sixths of the original apparent bulk. It might, perhaps, be thought to be due to a gradual slow solution of the supposed insoluble constituent, but this explanation is certainly incorrect. I suggest that the phenomenon in question is due to the india rubber solution acting like a solvent

vacuo, when it was obtained as a light-brown stringy mass, the bulk of which was almost infinitesimal compared with the volume it occupied during its preparation. In various operations the weight of the insoluble constituent obtained varied from 3 to 6·5 per cent., the average being about 3·5 per cent.

In india rubber solvents this substance swells to an enormous extent without any appreciable quantity passing into solution. The fibrous structure which thin sections of it exhibit under the microscope is not, as has been suggested, comparable with that of certain elementary animal or vegetable tissues, but appears to be the result of a peculiar process of shrinking of the drying substance, producing a reticulated appearance closely resembling that of some of the artificial colloidal structures described by BÜTSCHLI.[1] (*See* Frontispiece.)

This insoluble body, even when dilated by solvents, is entirely free from stickiness, and possesses no trace of that adhesiveness, or capability of interfusion, so characteristic of india rubber. When dry, it sh ws a remarkable degree of toughness, but very moderate distensibility. On analysis, its composition was found to correspond very closely to that of a body expressed by the formula $C_{30}H_{68}O_{10}$[2].

On the other hand, the analysis of the soluble part of india rubber without any further purification led to figures which revealed the presence of still nearly 2 per cent. of oxygen :—

	Found.	Calculated for $C_{10}H_{16}$.
C, ...	86·51	88·23
H, ...	11·59	11·76
O, ...	1·89	...

By redissolving this product in chloroform, diluting the solution so that it contains about 0·1 per cent. of india rubber, submitting this solution to a very careful fractional precipitation with alcohol, and rejecting the precipitate first obtained, a product of a high degree of purity resulted. The analysis of this product led to the figures :—

	Found.	Calculated for $C_{10}H_{16}$.
C, ...	87·91	88·23
H, ...	11·86	11·76

These agree very satisfactorily with the composition of a compound $C_{10}H_{16}$.

The two results are of extreme interest, and, to begin with, enable us to rectify the erroneous statement that the soluble and the insoluble con-

being deprived of its proper solvent, or swelling agent, contracts and becomes increasingly less in bulk, though not in weight. All those who have had a fair amount of experience regarding the behaviour of colloids in solution will have observed cases where a colloid, insoluble in a certain solvent, becomes soluble in the solution of another colloid in the same solvent.

stituents of india rubber are identical in their composition (isomeric). Our data further enable us to refute as incorrect the exaggerated figures quoted by various writers respecting the proportions of the soluble, and of the insoluble, constituents of india rubber; and it is, at the same time, quite evident that the proportion of the latter is on the average so small that it would be utterly futile to ascribe to it any important, or even distinctly traceable, function as regards the technical aspect of the physical properties of india rubber. We further see that GLADSTONE and HIBBERT's attempt to explain the presence of the insoluble part of india rubber as due to the action of heat upon the latter can no longer be accepted, although their statement regarding the general effect of heat upon india rubber is, no doubt, true.

The most remarkable fact concerning this insoluble portion is its high percentage of hydrogen, and the very large amount of oxygen it contains. By some kind of common consent the oxygen which is invariably present in technically pure india rubber has been ascribed to the oxidation of the india rubber by atmospheric oxygen. This notion is no longer tenable, as our above figures conclusively demonstrate that at any rate the bulk of the oxygen observed in india rubber is present in the form of the compound $C_{30}H_{68}O_{10}$, which, whatever it be, can scarcely be described as an oxidation product of india rubber. It appears to me that there exists an important genetic relationship between this compound and india rubber on the one hand, and the inosite, or inosite derivatives so commonly accompanying india rubber, on the other hand. This becomes, perhaps, even clearer by observing that

$$C_{30}H_{68}O_{10} = 3(C_{10}H_{16}) + 10H_2O.$$

In brief, I suggest that this insoluble compound is a link between india rubber and the complex carbohydrates, the celluloses in particular, which I am inclined to consider the raw material from which the plant produces all the terpenes, including india rubber.

There is, on the other hand, no doubt whatever that india rubber 'absorbs' oxygen when exposed to the atmosphere, and this oxygen absorption finally always results in the conversion of the india rubber into a brittle resinous body, generally described as SPILLER's resin. SPILLER has published an analysis of this body,[1] and gives the following figures:—

C, . . .	64·00
H, . . .	8·46
O, . . .	27·54

...ne

It is interesting to note that these figures very exactly agree with ...uent ...omposition of a body of the formula $C_{30}H_{48}O_{10}$, the relation of wh... ...ur insoluble constituent $C_{30}H_{68}O_{10}$ is obviously significant. ...s not to ...nteresting to observe is the fact, immediately deducible from ...es of india ...iven percentage composition of SPILLER's resin, that this oxi... any recognisable

rubber consists purely and simply in the addition of oxygen to the unsaturated india rubber molecule, and that consequently the carbon-hydrogen ratio of india rubber—10 : 16—remains unaffected in this process.

If we now examine the analytical figures, above given, of the soluble constituent of india rubber, before its further purification by fractional precipitation, we find at once that in this case also the carbon-hydrogen ratio is that of 10 : 16. From this we may infer that the oxygen percentage of india rubber in its resin free state of purity is due to two factors, one of which is the presence of the insoluble constituent $C_{30}H_{68}O_{10}$, the other the formation of oxygen addition products of india rubber.

The insoluble constituent does not seem to be present in all rubbers, but it appears that whenever it occurs it does so in rather small or infinitesimal quantities only. Whether its composition in the various brands of india rubber is the same as in Pará has not yet been ascertained, and will be a highly interesting subject for further enquiry. The statement I made, in the paper in which I first announced the composition of the insoluble constituent of Pará rubber,[1] that no corresponding body was to be found in any of the other varieties of india rubber, I can no longer maintain. The failure to find it in such rubbers as Lagos, Congo ball, Borneo, and Assam rubber was simply due to the fact that the examination was made on solutions obtained from these rubbers after they had been subjected to the process of washing in the roller mills generally used for this process. In this operation the insoluble body is disintegrated to such a degree that it no longer separates out from the solutions containing it, nor can it be isolated from them by filtration. It is there, nevertheless, but can only be obtained from solutions of the crude rubber. A preliminary examination of a large variety of commercial brands of india rubber in the crude state revealed the fact that nearly all appear to contain small but appreciable quantities of similar bodies. As showing again how comparatively insignificant is the amount of this insoluble body, I may already now call the attention of the reader to the tables below, which demonstrate the fact that the carbon-hydrogen ratio is for all varieties of india rubber practically a constant, very closely approximating the ratio 10 : 16. Considering the composition of the insoluble body, this is only possible if its quantity in every case is very small.

to 1 Already in the discussion of the composition of SPILLER's resin it has
·n pointed out that this product is formed by the direct addition of
being ·en on india rubber. We have seen further that the oxygen present
less in bu
regarding t soluble part of india rubber is not due to the presence, in a very
insoluble in a·divided state, of some of this insoluble constituent, but that the
same solvent. ·n combination with the rubber itself. In this case likewise
of the carbon-hydrogen ratio justifies the conclusion that

[1] BÜTSCHLI, ·U·
every student of the p.

[2] *Journn. Soc. Chem.*· Nature of India Rubber," *Journ. Soc. Chem. Ind.*, 1900.

this oxidation product is merely an addition product of india rubber and oxygen.

The following table shows that this is not only true of Pará rubber itself, but of all varieties of india rubber.

VARIETY.	C. Per Cent.	H. Per Cent.	O. Per Cent. 100 - (C + H).	C. : H.
Pará,[1]	87·87	11·51	0·61	10 : 15·7
Congo Ball,[2]	85·15	10·82	4·02	10 : 15·2
,, [1]	86·41	11·07	2·51	10 : 15·3
Borneo,[2]	86·63	10·83	2·53	10 : 15·0
,, [1]	87·76	11·23	1·00	10 : 15·3
Ceara,[2]	83·21	11·41	5·37	10 : 16·4
,, [1]	86·20	11·56	2·23	10 : 16·0
Lagos,[2]	86·11	11·54	2·34	10 : 16·0
Sierra Leone,[2]	86·38	11·34	2·27	10 : 15·7
Assam,[2]	87·17	11·47	1·35	10 : 15·8
Mangabeira,[2]	87·08	11·39	1·52	10 : 15·7
Cameta,[2]	85·41	11·09	3·49	10 : 15·5
Santos Sheet,[2]	83·56	10·90	5·35	10 : 15·6
Bahia,[1]	...	...	...	...
Beni River,[2]	85·55	11·46	2·98	10 : 16·1
Madagascar (Pinky),[2]	85·29	11·05	3·65	10 : 15·5
Balata,[2]	85·69	11·45	2·85	10 : 16·2
,, [1]	86·34	11·69	1·97	10 : 16·2
Gutta Percha,[2]	84·20	11·35	4·44	10 : 16
,, [1]	88·01	11·78	0·21	10 : 16

[1] Purified by extracting with acetone, dissolving in large volume of chloroform, and fractionately precipitating with absolute alcohol ; first fraction rejected.

[2] Purified only by thorough extraction with acetone.

These figures show clearly that a hydrocarbon of the formula $C_{10}H_{16}$ is the greatly preponderating constituent of all varieties of india rubber. The impossibility of completely removing all the oxygen from india rubber is of very little weight as an objection against this conclusion, seeing that every kind of india rubber subjected to a number of successive purifying treatments is obtained with an increasingly smaller percentage of oxygen until it reaches practically a vanishing point.[1]

The oxygen addition products contained in india rubber do not appear to sensibly affect the chemical behaviour of the whole, at least not so long as the percentages of oxygen so present remain within normal limits. This applies as much to the vulcanisation process of india rubber, which, as a chemical reaction, is rather badly defined, as to the derivatives we shall subsequently discuss. But this, of course, does not refer to the technically pure india rubber, which still contains the insoluble constituent and the 'oily and resinous matters.'

Considering the chemically inert nature of these impurities, it is not to be wondered at that their influence upon the chemical properties of india

[1] It is rather remarkable to observe that there appears not to exist any recognisable relation between the amount of resinous extract yielded by a sample of india rubber and its percentage of oxygen.

The amount of water absorbed by india rubber, although generally accepted to amount to approximately 25 per cent., has been found by various experimenters to vary considerably without, it is stated, any apparent reason. In this relation it should be pointed out that the absorption of water by india rubber depends very greatly upon the proportion of 'oily and resinous' matter contained in it. Indeed, by mixing india rubber with oils, resins, or waxes, its absorptive capability for water at once falls very considerably. Conversely, it increases by freeing the rubber of its resinous impurities by extraction with acetone.

The water absorption of vulcanised rubber is extremely small, certainly not large enough to appreciably affect the insulation of a rubber cable after five years' continuous immersion.

With *alcohol* india rubber behaves much as with water, the quantity absorbed averaging about 20 per cent.

Acetone swells the india rubber even more than alcohol, but without dissolving any trace of it.

All the *organic acids* slightly swell the india rubber, but are otherwise without any perceptible action.

Esters and *ethers* produce a swelling of the india rubber very much in excess of the similar action produced by any of the previously named solvents. This applies more particularly to ethyl ether, which is often, though erroneously, stated to be a solvent for india rubber.

The most important **solvents** of india rubber, approximately in the order of their rate of efficiency, are *turpentine* (*pinene*), *dipentene*, *petroleum spirit*, *carbon bisulphide*, *benzene* and its homologues, and *chloroform*. Of these, *petroleum spirit* and *benzene* and its homologues are especially notable on account of their technical importance. For the purposes of research a mixture of *carbon bisulphide* with 10 per cent. of *absolute alcohol*, and, more generally, *benzene* and *chloroform*, are especially suitable.

According to Hanausek,[1] the solubility of india rubber in various solvents is as follows:—

			Ceara.	Negrohead.	Sierra Leone.
100 parts of	ethyl ether	dissolve	2·6	3·6	4·5
,,	turpentine	,,	4·5	5·0	4·6
,,	chloroform	,,	3·0	3·7	3·0
,,	petroleum spirit	,,	1·5	4·5	4·0
,,	solvent naphtha	,,	4·4	5·0	4·7
,,	carbon bisulphide	,,	0·4	...	...

The solubility in benzene of various brands of india rubber is given by Heeren[2] as under:—

Guayaquil,	20	per cent.	Mozambique,	11·5	per cent.
Pará,	17	,,	Rangoon,	9·1	,,
Carthagena,	16·1	,,	Quiesembo,	9·0	,,
Borneo,	13·8	,,	Thimbles,	8·6	,,
African,	12·7	,,	Negrohead,	7·8	,,
Ceara,	12·0	,,	Madagascar,	5·7	,,

[1] *Jahresber. Chem. Tech.*, 1885, p. 1143. [2] *Polyt. Journ.*, 221, p. 391.

How the solubilities in the above two tables, which are everlastingly quoted, have been arrived at, I have not been able to ascertain, not having seen the papers of the two authors *in extenso.* I have, however, no hesitation in describing these figures as misleading and altogether erroneous, for the simple reason that, as far as my very numerous observations go, india rubber possesses *no solubility at all in the generally accepted sense* of this term. India rubber is either insoluble in a given medium, or, if 'soluble,' it is so in absolutely all proportions. Nor do any of these authors seem to have observed the fact that the 'solubility' of india rubber, which in this case simply means the degree of ease with which it passes into solution, depends very greatly upon the condition under which it is subjected to the action of the solvent. The 'solubility' of crude (though dry) india rubber in its original state is always very much slower than that of the same rubber after it has been washed, and the longer the india rubber has been subjected to the operations known as masticating, rolling, or kneading, the more rapidly does it pass into solution.

But under whatever conditions india rubber is subjected to solvents there is *no definite solubility,* for the simple reason that such a thing as *saturation does not exist in india rubber solutions, only concentration or* dilution. Indeed, the actual fact is that such a thing as an india rubber solution does not, strictly speaking, exist. *India rubber 'solutions' are not solutions of india rubber in a solvent, but solutions of a so-called solvent in india rubber*—a distinction with a considerable difference.[1]

If we place a piece of india rubber—for the purpose of this experiment preferably masticated india rubber—in one of its 'solvents,' the rubber does not pass into the solvent, but the latter passes into the former, swelling it very greatly, permeating every part of it, and forming a colloidal jelly. On adding more of the solvent, the same process repeats itself until, very gradually, we reach a point when the jelly begins to flow. On the addition of fresh quantities of 'solvent' to this jelly, the latter tends to separate from the liquid employed as oil from water, and only very gradually does the latter enter into and further distend the jelly; whereas, if normal solution took place, we should expect to see the jelly melting away into the liquid. But the whole process is of an exactly opposite character. This becomes strikingly apparent if we add to such a jelly a further quantity of solvent and stir vigorously. In this case we obtain at first an apparently thin solution, which, however, on close examination, will be found to possess all the characteristics of a gross emulsion of the jelly in the solvent. On continuing the agitation, the apparent thin solution rapidly begins to thicken, often giving one the impression that the addition of more solvent had actually resulted in producing a more viscous 'solution' than we possessed before this dilution. By the time the jelly has been distended with solvent to such an extent as to represent the analogue of about a 4 per cent. solution, we have reached such a degree of fluidity that further

[1] The same, indeed, applies, *pari passu,* to all the so-called solutions of colloids.

additions of the solvent *appear* to mix at once homogeneously with the whole solution.

GLADSTONE and HIBBERT[1] observed that heating reduces the solubility[2] of india rubber. If, however, the heat be applied to it in conjunction with a mechanical kneading treatment, its solubility vastly increases. Thoroughly 'masticated' india rubber does not take as many hours to dissolve as the crude product requires days.

The cause of this extraordinary physical behaviour is not at present understood, although we know that neither the application of heat by itself to india rubber, nor the combined influence of heat and mechanical working, induce any perceptible chemical change.[3] The physical change is, however, marked enough. It finds expression, as already remarked, in the much increased solubility of the product, and also in the increase of its plasticity at the expense of its elasticity. This change becomes the more marked the longer the rubber has been mechanically worked. But these observations, upon which rest important technical applications, are

[1] *Journ. Chem. Soc.*, 1888, p. 679.

[2] By this term, here and in future, as applied to india rubber, I mean simply to designate the relative ease of forming a pseudo-solution.

[3] This statement might be called in question in view of the fact, well known to practical workers, that the longer india rubber has been worked mechanically, the more sulphur it requires for vulcanisation. It must be borne in mind, however, that to the manufacturer the term 'vulcanisation' denotes merely the physical aspect of the change produced in india rubber by sulphur at higher temperatures. The discovery that this physical change is due to the formation of an addition product of india rubber and sulphur is of quite recent date, and even at present there are still some workers who either altogether deny the formation of such compounds, or, if they admit it, consider it as without influence upon the physical result of the vulcanisation. Therefore, if the manufacturer describes a certain article as vulcanised, he does so merely upon the evidence of its physical properties, without any regard as to whether this article contains any free sulphur, and—if so—how much, or whether it does not. Now, while in the author's opinion this book furnishes conclusive proof that the vulcanisation is the physical effect of the chemical combination of india rubber and sulphur, the degree of the physical effect thus produced is, however, a rather complicated function of the amount of sulphur combined with the india rubber (sulphur of vulcanisation), and of the physical state of the india rubber when subjected to vulcanisation. While, therefore, for india rubber in the same physical condition the physical vulcanisation effect increases proportionately with the amount of combined sulphur, equal quantities of combined sulphur in different samples do not necessarily imply physical equality of vulcanisation. In the latter respect two chemically equivalent samples differ according to the difference of the physical conditions of the india rubber from which respectively the two vulcanised samples were obtained. A highly interesting application of this fact is to be found in the manufacture of ebonite (hard rubber). For the manufacture of this product the india rubber is mechanically worked into a state of complete plasticity, almost entirely destroying its elasticity. Vulcanisation is then effected with a very large quantity of sulphur, yielding a tough, highly elastic product. If the india rubber were as little worked as is customary for the manufacture of soft rubber goods, the high degree of vulcanisation would result in the production of a very hard, but extremely brittle, product. In other words, the great physical difference between rubber worked for varying lengths of time does not appreciably affect its chemical behaviour towards sulphur, although it greatly influences the physical effect of the vulcanisation.

as yet quite unaccounted for. So is also the well-known fact that the mechanical strength of india rubber which has once been dissolved is greatly inferior to that of the crude rubber, a difference which even persists after vulcanisation, and which finds expression in the universal commercial distinction of cut sheet rubber as against 'spread sheet rubber,' and between the goods manufactured from either of them.

It is not surprising that these facts, in conjunction with the observation that rolled (calendered) sheets of india rubber show a considerable difference in **tensile strength** in the directions respectively of the length and width of the sheet, should have given rise to the opinion that india rubber possesses something akin to the warp and weft structure of a textile fabric. Indeed, this crude analogue may yet be found to have some foundation in an ultimate definite disposition of the molecules of all colloids in the plastic state at right angles to any strain acting upon the colloidal aggregate. It is certainly very curious that all colloids, which in the plastic state are formed into films, should possess considerably greater strength across the sheet or film than along it.

To the unaided eye india rubber, as all other colloids, appears quite structureless. The reticulated structure attributed to it by Payen is perhaps due, not so much to its porosity, as to a particular form of distribution throughout its mass of the above mentioned insoluble constituent. Wiesner[1] has also observed this reticulated structure in some kinds of india rubber, but certain varieties he found to be entirely without.

All varieties of india rubber, viewed under the polarising microscope, exhibit brilliant **interference colours**, particularly if thin sections are strongly compressed between two slides.

According to Exner, india rubber possesses 'perfect **elasticity**.' But this statement is, to say the least, certainly misleading. It is neither true of crude nor of manufactured (vulcanised) india rubber, and is probably only another instance of the incorrect way in which the word 'elastic' is so often used, by none more so than by rubber manufacturers themselves. In scientific terminology that substance is regarded as having the highest coefficient of elasticity which requires the greatest stress to produce a given deformation or strain. Thus, the hardest steel is more perfectly elastic than a piece of india rubber, but it is certainly not so stretchable or distensible.

The distensibility of india rubber increases considerably with the temperature, and is, in the crude product, the same in every direction. It appears so far to have escaped observation, that, on distension, india rubber acquires a strong negative electric charge—*i.e.*, loses electric potential. This interesting phenomenon can easily be observed by stretching over an ordinary gold-leaf electroscope a small sheet, preferably unvulcanised, of pure india rubber. On removing the sheet while still in the stretched condition, the leaves will be found to diverge widely. On releasing the

[1] Wiesner, *Rohstoffe*, 2nd ed., 1900, 386.

stretched sheet, it returns, of course, to its original condition, and the potential becomes normal. On exposing distended india rubber to low temperatures, the distension remains permanent at ordinary temperature, but gradually disappears on heating. URE found the specific gravity of india rubber in the normal and in the distended condition to be 0·9259 and 0·9487 respectively. On first heating india rubber in the distended condition to 115° C. and then cooling it, no contraction occurs, and the distension is rendered permanent.

Not unconnected with the above described electrical phenomenon accompanying the distension of india rubber is probably the fact, observed by JOULE, that distension is accompanied by the **evolution**, and contraction by the **absorption**, of **heat**. In agreement with this is the observation due to TYNDALL that india rubber, distended to three times its length, contracts on warming. On closer examination of this phenomenon, SCHMULEWITSCH showed that this contraction occurs only if a considerable load is attached to the india rubber: under a light load further distension takes place on the application of heat. Accordingly, there exists an intermediate load, under which the degree of distension of india rubber remains constant at various temperatures.

On submitting unvulcanised india rubber to heat, its softness and stickiness increases, it becomes more plastic. Subjected to low temperatures, it grows very stiff, almost horny. This behaviour is considerably altered by vulcanisation, the effect of which is to render the physical properties of india rubber almost indifferent to temperature changes within the interval of from 0° C., or even somewhat lower, to 100° C. On immersion, however, into boiling liquid air, even vulcanised india rubber becomes hard and as brittle as glass.

The rate of diffusion of different gases through india rubber septa was found as follows by GRAHAM[1]:—

Nitrogen,	1	Oxygen,	2·556
Carbon monoxide,	1·113	Hydrogen,	5·500
Air,	1·149	Carbonic acid,	13·585
Methane,	2·148		

GRAHAM, whose experiments in this direction were based upon corresponding observations made by DR MITCHELL of Philadelphia, suggested that "those gases penetrate most readily which are easily liquefied by pressure, and which are also generally highly soluble in water or other liquids," and he assumes that the gases entering into the rubber septum are liquefied in it, permeate it, and are again evolved on the other side.

WROBLEWSKI arrived at the following conclusions in an investigation on the **absorption of gases**:—

1. Henry Dalton's law for the absorption of liquids and gases applies also to india rubber and gases.

2. The absorption coefficients of vulcanised india rubber are linear

[1] *Phil. Trans.*, 1866, 399.

functions of the temperature; they decrease with increasing temperature for nitrous oxide and carbonic acid, but the absorption coefficient for hydrogen increases with the temperature.

3. The absorption of nitrous oxide, carbonic acid, and hydrogen is a purely physical phenomenon involving no chemical reaction.

4. Graham's hypothesis assuming the liquid condensation of the gases within the india rubber is untenable.

5. The absorbed gases persist in the gaseous state and retain all the properties characteristic of the latter.

6. The gases distribute themselves through the india rubber, according to the laws of thermal conductivity of solid bodies, which laws apply also to the absorption phenomena of all substances.

7. The constant *D*, of nitrous oxide, carbonic acid, and hydrogen is independent of the chemical nature of the gases, and also of their coefficients of absorption and saturation.

8. It depends only upon the physical properties of the gases, their specific gravities more particularly. Approximately it varies inversely as the square roots of their specific gravities, with this exception, however, that the specifically very light gases possess a much greater constant than what would follow from the above relation.

9. In the case of nitrous oxide and carbonic acid the constant *D*, increases with the temperature.

10. At 10° C. it amounts for these gases to about 0·02 of the corresponding value for carbonic acid and water.

11. An india rubber septum acts like a porous plate, possessing the property of condensing gases. The porosity of india rubber is of the same order as that of solid graphite.

12. From Graham's experiments it may be inferred that also in heated metals the constant *D*, is smaller for the gases of lower specific gravity.

In a series of experiments on grey vulcanised india rubber, Hüfner[1] arrived at the following conclusions:—

1. Within a range of temperatures from 5 to 25° C. there is no definite absorption coefficient of india rubber for air. The apparently existing absorption is an absorption of oxygen only, causing probably the oxidation of the india rubber.

2. Within a range of temperatures from 15 to 25° C. india rubber absorbs no measurable quantities of nitrogen, and the same is true of

3. Hydrogen within a range of temperatures from − 2 to + 13° C.

4. On the other hand, at a temperature of − 2° C. india rubber absorbs its own volume of carbonic acid.

Zulkowski has shown that the absorption of ethylene and of the higher aromatic hydrocarbons of coal gas is sufficiently marked to interfere with the illuminating power of the gas. India rubber is able to absorb 8·64

[1] *Ann. Phys. Chem.*, N.F. [34], 1.

per cent. of its weight of these gases. It must, however, be pointed out that these gases, when liquefied, are all energetic solvents of india rubber, and this absorption is therefore equivalent to the absorption of water vapour from the air by hygroscopic substances.

Regarding the **molecular weight** of india rubber nothing of any definite nature is known at present. Its statistical formula, on the basis of the best analyses made with the most highly purified products obtainable, may safely be accepted as $C_{10}H_{16}$, but is very probably many times larger. It cannot be smaller, for, although C_5H_8 would express its percentage composition equally well, GLADSTONE and HIBBERT [1] have shown (*see* page 23) that for $C_{10}H_{16}$ india rubber contains three ethylene bonds. From the behaviour of india rubber against sulphur monochloride, the author [2] has deducted the formula $C_{50}H_{80}$ as a possible minimum, and certain other chemical facts since discovered have rendered this formula, or, as an alternative, $C_{60}H_{96}$ as well within the range of possibilities, without, however, settling this important point.

GLADSTONE and HIBBERT [3] attempted to ascertain it by determining the depression of the freezing point of a 10 per cent. solution of india rubber in benzene, but the observed depression was so exceedingly small, that if RAOULT's law holds good in this case, the molecular weight of india rubber would appear to be of enormous magnitude.

Action of Heat upon India Rubber.

Under the influence of comparatively moderate degrees of dry heat the tackiness of all brands of india rubber increases more or less rapidly, but no comparative investigation of the softening effect of heat upon the different brands has been made. It is, however, well known in rubber works that certain brands of india rubber cannot be hung up to dry in the form of sheets after the washing process, as they become so soft as to fall to pieces. It must not be supposed, however, that this softening of technically pure rubber is a property of the india rubber hydrocarbon itself absolutely. In commercial qualities of india rubber the resinous and oily substances all possess very low melting points; in many cases, indeed, they are liquid or semi-liquid at ordinary temperatures. At higher temperatures they act upon the india rubber as solvents, and in this manner often greatly exaggerate what might seem to be the softening action of heat upon india rubber. For this reason the temperature at which any given brand of india rubber begins to soften or melt can only be stated within very wide limits, as it varies for the same brand according to the percentage of resins present. Indeed, india rubber has no true melting point. With the rising temperature it grows softer and stickier, reaching sooner or later a condition in which it can no longer be handled without adhering to everything

[1] *Journ. Chem. Soc.*, 1888, p. 682.
[2] *Journ. Soc. Chem. Ind.* [xv.], 1894, p. 16.
[3] *Journ. Chem. Soc.*, 1888, p. 691.

it touches, and eventually it passes into a more or less fluid state. The point at which this occurs is generally stated to lie at a temperature of about 170 to 180° C. This, however, refers probably to india rubber (Pará) containing its usual amount—1·5 per cent.—of oily and resinous matter. The melting point of india rubber purified by extraction with acetone certainly lies much higher. GLADSTONE and HIBBERT[1] found that on heating a solution of pure Pará in toluene to 200° C. for two hours, and then distilling off the solvent at 112° C., there was left a residue of absolutely unaltered india rubber. Even when heated at 210° C. in a Sprengel vacuum, the india rubber was found to be only superficially melted, though after that treatment it dissolved very slowly in benzene.

The combined action of heat and mechanical working upon india rubber is much more marked, and it is of considerable technical importance. It has, generally speaking, the effect of gradually increasing its plasticity and adhesiveness at the expense of its elasticity and cohesion. This effect is very curious and cannot be explained by the absorption of oxygen by the india rubber during the treatment, as this amounts to only from 0·5 to 1 per cent. If this oxidation is prevented by carrying out the whole operation in an atmosphere of carbonic acid, the result is still the same. More remarkable still is the fact that the longer the above treatment is continued, the greater is the amount of sulphur required to obtain a certain mechanical standard of vulcanisation, or, in chemical terms, the higher is the amount of combined sulphur required in the india rubber in order to produce a solid and stable vulcanisation product. For this reason it is obvious that in the production of soft rubber goods the india rubber should be worked as little as possible; whereas, for the production of hard rubber, the longer it is worked, the better for the purpose. MINDER's statement[2] that articles produced from 'long worked' india rubber are liable to decay rapidly is therefore entirely misleading; they are so only if the degree of vulcanisation has not been adapted to the altered physical conditions produced in the india rubber. But this is equally true of india rubber in any other condition.

Although no perceptible decomposition takes place at the temperature given above, india rubber liquefied at this temperature is found to have undergone a great change. On cooling, it remains very soft and sticky, and although on long standing it may return to a more solid condition, the former elasticity of the india rubber has disappeared, and it exhibits now a brittleness much resembling that of certain kinds of bitumen. To account for this remarkable change, HEINZERLING[3] suggests that the conversion of the india rubber into a tarry mass by heat may be a process similar to the conversion of starch into starch paste. This analogy is, however, too superficial; it barely expresses the physical aspect of the observed facts, and it is either inadequate or misleading if applied to the explanation of

[1] *Journ. Chem. Soc.*, 1888, p. 686. [2] *Gummi Zeitung*, 14, 687.
[3] *Fabrik. der Kautschuk- und Gutta-Percha-Waaren*, Braunschweig, 1883.

the chemical aspect of the change in question. For whereas the process of the liquefaction of starch is a hydration process dependent upon the interaction of starch and water under the influence of higher temperature, the liquefaction of india rubber under the influence of heat involves no chemical reaction ; it is most likely due to a physico-chemical or molecular change comparable to the conversion of paraldehyde into aldehyde. In other words, the liquefaction of india rubber is probably due to the breaking up of the no doubt very large india rubber molecule into smaller molecules of the same empirical formula. This is shown by the fact, which will be dealt with in detail later on, that india rubber in its primary state, as well as after liquefaction, at any temperature up to 200° C., and even the products of the dry distillation of india rubber, all possess the empirical formula $C_{10}H_{16}$, and form a bromine addition product $C_{10}H_{16}Br_4$. But there is this difference between these conversion products and india rubber, that the higher the temperature at which they have been formed, the more soluble and the more reactive they are, and this also holds good for the bromides of these conversion products as compared with the bromide obtained direct from india rubber. Now this break up of the india rubber molecule is carried to its extreme limits in the dry distillation of india rubber. This has been investigated, with highly interesting results, by a number of observers. Nevertheless, the subject is one still inviting research, and, even as far as it has been dealt with, one that requires revision in a number of points.

The dry distillation of india rubber was first investigated by Himly,[1] at almost the same time as by Bouchardat.[2] But no more recent investigation than that of Williams[3] in 1860 appears to have been made. From the distillation products three definite compounds were isolated : isoprene C_5H_8 (B.P. 37–38° C.), caoutchene $C_{10}H_{16}$ (B.P. 171° C.), and heveene (B.P. 315° C). According to Bouchardat, the crude distillate also contains a butylene C_4H_8 boiling at between − 18 and 0° C. Five kilos of fresh Pará rubber yield, besides a small quantity of gases, 250 grms. of isoprene, 2000 grms. of caoutchene, and 600 grms. of heveene. The rest consists of very heavy oils possessing very high boiling points. There is, however, no doubt that these yields depend largely upon the conditions under which the distillation is carried out, although the qualitative products remain the same in every case. Now, while this shows that the production of the above named bodies in the dry distillation of india rubber does not indicate three or more different lines of cleavage in the molecule of the latter, it points very distinctly towards the assumption that these three or more compounds stand in close genetic relation to each other. If we disregard the observation of Bouchardat that a small quantity of butylene is formed in the dry distillation of india rubber, an observation which, so far, has not been confirmed, we find that all the characteristic products formed in this

[1] *Ann. Chem.*, 27, 41. [2] *Bullet. Soc. chim.*, 24, 108.
[3] *Proc. Roy. Soc.*, 10, 517.

process are characterised by the same percentage composition, and their respective molecular complexes by the general formula $(C_5H_8)_n$, which also includes the mother substance, india rubber itself. This consideration renders it highly improbable that any of the above named compounds are immediate products of the destructive distillation of india rubber, but rather suggests that they are all due to the disintegration of larger molecules. With regard to isoprene, this is scarcely open to doubt, inasmuch as TILDEN[1] showed it to be one of the products of the destructive distillation of various terpenes. The fact that of the above named bodies only isoprene, and neither caoutchene nor heveene, is capable of polymerisation into india rubber[2] renders the existence of the hexane ring, in the molecule of the latter at least, very doubtful. But this doubt becomes a certainty in the light of the results obtained by GLADSTONE and HIBBERT[3] in the optical examination of india rubber. In investigating the optical properties of india rubber, taking $C_{10}H_{16}$ as the molecule of this compound, these authors desired to ascertain whether the $C_{10}H_{16}$ molecule of india rubber contains one, two, or more pairs of doubly linked carbon atoms.

"The theoretical refraction and dispersion equivalents of $C_{10}H_{16}$ in the three conditions above mentioned would be as follows, assuming that each pair of doubly linked carbon atoms would produce the same increment as in the aromatic series":—

$C_{10}H_{16}$	$P\frac{\mu_A - 1}{d}$	$P\frac{\mu_H - \mu_A}{d}$
1 pair of doubly linked carbons, ...	73·0	4·0
2 ,, ,, ,, ...	75·2	4·8
3 ,, ,, ,, ...	77·4	5·6

GLADSTONE and HIBBERT found that the **optical constants** of india rubber exhibit considerable variations in different specimens. These variations appear to be in direct proportion of the amount of oxygen present, which, it is safe to assume, attaches itself to the doubly linked carbon atoms present, thereby suspending the double bond and lowering both the refraction and dispersion equivalents. However, two especially carefully prepared samples yielded the following figures on examination:—

Sample.	$P\frac{\mu_A - 1}{d}$	$P\frac{\mu_H - \mu_A}{d}$
No. 10,[4]	76·87	5·67
No. 11, ...	77·59	5·34

These figures leave little doubt that india rubber, for $C_{10}H_{16}$, contains three pairs of doubly linked carbon atoms.

"If this be the case, the molecular formula cannot be C_5H_8 like isoprene, or $C_{15}H_{24}$ like citrene, as these would give respectively one and a half, and four and a half, pairs of carbon atoms united by double linking.

[1] *Trans. Chem. Soc.*, 45, 410. [2] TILDEN, *Chem. News*, 1892, p. 265.

[3] *Journ. Chem. Soc.*, 1888, p. 680.

[4] These numbers are taken from the experimental series given in the authors' repeatedly quoted paper.

It cannot contain the hexagonal ring,[1] but must be expressed graphically by a chain formula. This may account for the wide difference of properties between caoutchouc and the various essential oils.

"The general results of the destructive action of heat upon caoutchouc may therefore be considered as involving no change in the proportion of carbon to H, but changes of structure in the hydrocarbon which are best represented by the following optical constitutional formulæ. In this table C'' is used for C, having the refraction equivalent 6·1 and the dispersion equivalent 0·66":—

Substance.	Optical Constitutional Formula.
India rubber (polyprene), ...	$_{n}\,C''_6C_4H_{16}$
Isoprene, ...	C''_4CH_8
Caoutchene (dipentene), ...	$C''_4C_6H_{16}$
Heveene, ...	$_{n}\,C''_2C_3H_8$

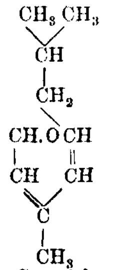
One is forcibly reminded by these facts of the very similar type of reactions exhibited by a well-known camphor, geraniol, and geranial, its aldehyde. Geraniol has been shown to possess the formula $C_{10}H_{18}O$

$$(CH_3)_2CH.CH_2.CH:CH.C(CH_3):CH.CH_2(OH).$$

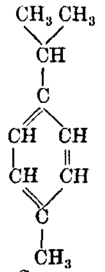
On oxidation with bichromate it yields an aldehyde, geranial, $C_{10}H_{16}O$

$$(CH_3)_2CH.CH_2.CH:CH.C(CH_3):CH.CHO,$$

and this, on treatment with dehydrating agents, splits off water with formation of cymene. This transformation is an exact parallel to the formation of dipentene and heveene in the destructive distillation of india rubber. We have at any rate here the same transformation of an olefinic carbon chain (geranial) into a derivative of a cyclohexane. This process, in its application to the india rubber problem, is so interesting that it is worth while illustrating more clearly the formation of the hexane ring from the open chain. This is best done by the following graphical representation:—



Geranial.



Cymene.

In its results upon the optical constants of the two compounds this process is, however, exactly the reverse to what we observed in the case of india rubber. It will, of course, be observed that this is simply due to the fact

[1] The exactly contrary statement in the article "India Rubber," in vol. i. p. 311 of *Thorpe's Dict. of Appl. Chem.*, is obviously a misquotation by the compiler of that article.

that in the case of geranial the ring formation is not due, as in the case of india rubber, to a physical rearrangement of carbon bonds, but to a dehydration process which results in the formation of a benzene derivative as distinguished from a terpene.

Now, if we apply to geraniol the same process of dehydration which from geranial led to cymene, it is obvious that we should obtain a compound $C_{10}H_{16}$, a terpene. This important experiment was carried out by SEMMLER,[1] and resulted in the formation of an undoubted terpene. The optical analysis of this terpene, geraniene, indicated the existence in it of three ethylene bonds, full proof of which was furnished by the formation of an addition product $C_{10}H_{16}Br_6$. This shows that in geraniene we have a terpene which stands evidently in the same relation to india rubber as the monocyclical terpenes to the polyterpenes. Just as there is a homologous series of cycloterpenes, the terms of which differ from each other by an increment C_5H_8, and all of which answer the general formula $(C_5H_8)_n$, so also there is, no doubt, a series of olefinic or open chain terpenes,[2] of which geraniene and india rubber are extreme terms.

The connecting link between these two series is the hemiterpene isoprene C_5H_8, which on polymerisation may, and indeed does, form simultaneously representatives of both series; for we know already that in the polymerisation of isoprene, india rubber, the olefinic polyterpene, is formed at the same time as the cycloterpene dipentene.

The constitution of this connecting link, isoprene, has long been doubtful, but has recently been elucidated by IPATIEFF and WITTORF.[3] Already TILDEN,[4] however, came to the conclusion that the constitution of isoprene would most probably have to be expressed by the graphical formula $CH_2 = C(CH_3) - CH = CH_2$, which compound he described as β-methylcrotonylene, although he did not succeed to furnish experimental proof for this assumption. WALLACH'S[5] investigations thoroughly confirmed BOUCHARDAT'S[6] and TILDEN'S results, and he further established the perfect identity of the terpene $C_{10}H_{16}$, formed by the polymerisation of isoprene with cymene (dipentene).

The first approach towards experimental confirmation of TILDEN'S formula of isoprene was, however, furnished by GADZIATZKY,[7] who from the monochlorhydrate of isoprene obtained a tertiary alcohol

$$\begin{matrix} CH_3 \\ CH_3 \end{matrix} \rangle COH - CH = CH_2$$

dimethyl-vinylcarbinol. Soon afterwards the same author[8] found that,

[1] *Ber.*, 24, 682.

[2] With the exception of india rubber, no higher term of the olefinic terpene series is known at present than $C_{10}H_{16}$, but several isomers of this formula and series are already known.

[3] *Journ. prakt. Chem.* [2], 55, p. 1, 1896.

[4] *Chem. News*, 46, 129.

[5] *Ann. Chem.*, 227, 292.

[6] *loc. cit.*

[7] *Bull. Soc. chim.* [2], 47, 168.

[8] *Journ. russ. chem. Ges.*, 20, i. 706.

on heating with weak alcoholic hydrochloric acid, isoprene is transformed into an isomeric dimethyl-allene, which transformation he expressed graphically thus:—

$$CH_2=CH-C\begin{matrix}\diagup CH_3\\ \diagdown CH_2\end{matrix}+HCl = CH_2=CH-\underset{\displaystyle Cl}{\underset{|}{C}}\begin{matrix}\diagup CH_3\\ \diagdown CH_3\end{matrix}$$

$$CH_2=CH-\underset{\displaystyle Cl}{\underset{|}{C}}\begin{matrix}\diagup CH_3\\ \diagdown CH_3\end{matrix}-HCl = CH_2=C=C\begin{matrix}\diagup CH_3\\ \diagdown CH_3\end{matrix}$$

So far all the addition products of isoprene obtained by the above named authors are liquids possessing somewhat indefinite physical characteristics, and more or less prone to decomposition on distillation. But in 1895 MOKIEWSKY[1] succeeded to obtain a solid crystalline body (M.P. 81° C.) by the action of hypochlorous acid upon isoprene. The empirical formula of this substance was found to be $C_5H_{10}O_2Cl_2$. Besides this solid body, which he regarded as an addition product of two molecules of hypochlorous acid with one molecule of the hydrocarbon C_5H_8, he obtained a liquid (B.P. 141° C.), the analysis of which led to the formula $C_5H_{11}OCl$, and which, on treatment with alkali, yielded trimethyl-ethylene oxide and a glycol. From this MOKIEWSKY inferred that in the distillation of pinene through red-hot tubes, by which process he had obtained the raw material for his investigation, a mixture of trimethyl ethylene $(CH_3)_2C=CH.CH_3$ and of a hydrocarbon C_5H_8 is obtained, the latter constituting the bulk of the distillate.

This fact must appear particularly interesting since IPATIEW and WITTORF[2] succeeded in isolating trimethyl-ethylene also from the products of the dry distillation of india rubber. The hydrocarbon C_5H_8 accompanying it, they isolated in the shape of a dihydrobromide of the formula $C_5H_{10}Br_2$, and this substance was found to be identical with the dihydrobromide obtainable from the above mentioned β-dimethyl-allene. This led the authors to conclude that the hydrocarbon C_5H_8, isoprene, must possess the constitution of a β-methyl-divinyl, as only such a compound could be expected to yield the same dihydrobromide as the unsymmetrical dimethyl-allene. This will become perfectly clear by a perusal of the following graphic representation:—

$$\begin{matrix}CH_2\diagdown\\ CH_3\diagup\end{matrix}C-CH=CH_2+2HBr = \begin{matrix}CH_3\diagdown\\ CH_3\diagup\end{matrix}CBr-CH_2-CH_2Br$$

Isoprene (β-methyl-divinyl) — Dimethyl-trimethylene-bromide.

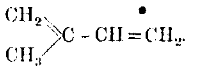
$$\begin{matrix}CH_3\diagdown\\ CH_3\diagup\end{matrix}C=C=CH_2+2HBr = \begin{matrix}CH_3\diagdown\\ CH_3\diagup\end{matrix}CBr-CH_2-CH_2Br$$

β-dimethyl-allene. — Dimethyl-trimethylene-bromide.

In completing his proof of the constitution of isoprene, IPATIEW[3] shows

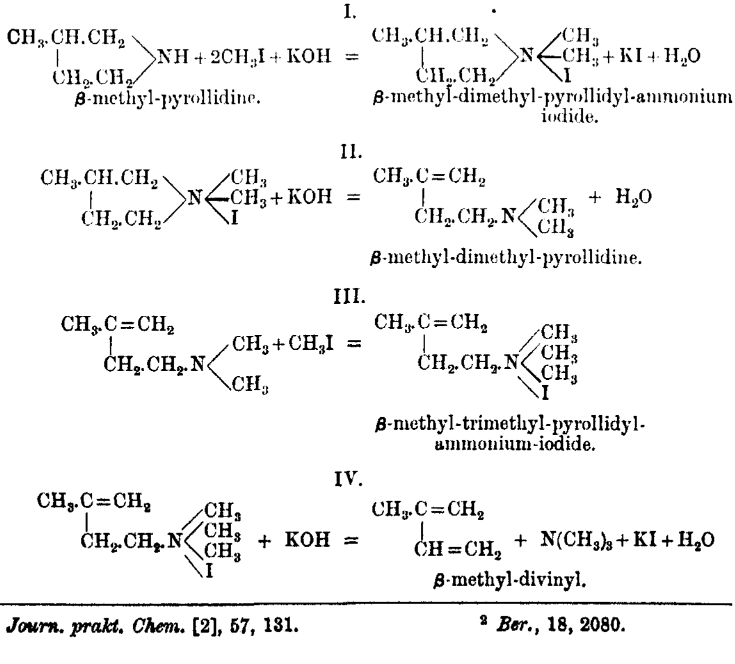
[1] *Journ. russ. chem. Ges.*, 27, 516.
[2] *Journ. prakt. Chem.* [2], 55, 1.
[3] *Ibid.* [2], 55, 4.

that the action of alcoholic potash upon dimethyl-trimethylene-bromide, whether prepared from isoprene or β-dimethyl-allene, always yields the same hydrocarbon, boiling at from 32 to 33° C. This remarkably low boiling point of this hydrocarbon (C_5H_8), as well as its other properties, altogether preclude the assumption of its constitution being that of either a secondary or di-substituted acetylene, nor of β-dimethyl-allene, so that there remains for isoprene only the formula of β-methyl-divinyl,



That the peculiar distribution of the ethylene bonds in methyl-divinyl must actually exist in isoprene, he proves, not only by the identity of the dihydrobromide of isoprene with the dihydrobromide of allene, but more particularly by the fact of it producing with hypochlorous acid a dichlorhydrine, a property very characteristic of hydrocarbons of the diallyl type.

The final proof of the identity of isoprene with β-methyl-divinyl was subsequently furnished by EULER,[1] who succeeded in preparing β-methyl-divinyl synthetically, and found it in all its remarkable properties identical with isoprene. He used as his starting-point the observation of CIAMICIAN and MAGNAGHI,[2] that dimethyl-pyrollidyl-ammonium-iodide on treatment with caustic potash yields divinyl. There being a β-methyl-pyrollidine known, it was to be expected that this substance could be similarly converted into β-methyl-divinyl. This he accomplished by the following reactions:—



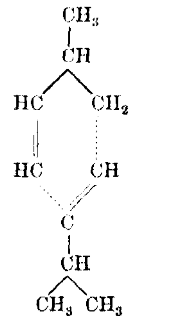
[1] *Journ. prakt. Chem.* [2], 57, 131.

[2] *Ber.*, 18, 2080.

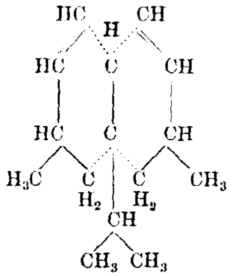
The β-methyl-divinyl so obtained is in every respect identical with isoprene, the constitution of which is therefore definitely established.

I have dwelt upon this matter of the constitution of isoprene to an extent which might, perhaps, appear rather beyond the scope of this book. But I would point out that this book, although purporting to be an analytical treatise, is also intended for the use of those to whom india rubber is more than a raw material for technical purposes, and to those an account such as the above will appear deeply interesting and even helpful.

It has been already repeatedly stated that isoprene under various conditions may be polymerised again into india rubber, which process is, however, invariably accompanied by the polymerisation of a considerable part of it into a cycloterpene, sesquiterpene, and even higher members of the cycloterpene series. The process is no doubt a very complicated one, and is entirely unknown how, and what description of, an open chain is formed representing india rubber. All we can say on this point is that no configuration containing cyclical rings of any sort would result in a product, the configuration of which, as regards the number of ethylene bonds in the $C_{10}H_{16}$ unit, could be brought into accordance with the above quoted results of the refraction equivalent of india rubber. The manner in which isoprene can polymerise into derivatives of the cycloterpene series is, however, quite obvious, and will readily be seen from the two following diagrams,



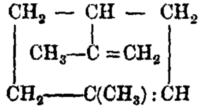
Terpene $C_{10}H_{16}$.



Sesquiterpene $C_{15}H_{24}$.

in which the dotted bonds show the junctions of one molecule to the other. It will be observed that even polymerisations such as these are very complicated processes indeed, involving a peculiar process of migration of hydrogen atoms.

By far the bulk of the products of the destructive distillation of india rubber consists of the well-known cycloterpene known as dipentene, the constitution of which may be expressed graphically :—



Δ''^{3}—Terpadiëne.

Besides occurring naturally in various essential oils, it may be obtained in

a variety of ways from either certain terpenes or terpene derivatives. The boiling point of dipentene, the caoutchene of the older literature, was observed by WALLACH at 178° C.,[1] its specific gravity as 0·845. Dipentene is optically inactive, and as all its derivatives can also be prepared by mixing together equal quantities by weight of the corresponding derivatives of leavo- and dextro-limonene, it follows that dipentene is the racemic modification of limonene.

A rather considerable proportion of distillate yielded by the dry distillation of india rubber consists of heveene $C_{15}H_{24}$, a sesquiterpene, B.P. 255–265° C. Its constitution, like that of the sesquiterpenes in general, is still quite unknown. It certainly cannot be that of the sesquiterpene figured on page 28, since GLADSTONE and HIBBERT showed heveene to contain one pair of doubly linked carbon atoms for C_5H_8.

The very considerable remaining part of the india rubber distillate consists of bodies boiling above 300° C. These bodies are not only, like the lower boiling fractions, hydrocarbons, but their composition still conforms to the formula $(C_{10}H_{16})_n$. They are therefore, no doubt, diterpenes, and perhaps even in part still higher polyterpenes. For the disentanglement of mixtures of this description our present methods are ineffective.

The amount of carbon remaining behind on the destructive distillation of india rubber is surprisingly small—indeed, so small as to suggest that it is more due to its albuminous and other impurities than to the india rubber itself. From 3 kgms. of carefully washed and vacuum-dried india rubber (Pará) I obtained :—

Isoprene,	186 grms.	= 6·2	per cent.[2]
Dipentene,	1380 ,,	= 46·0	,,
Heveene,	510 ,,	= 17·0	,,
Polyterpenes,	806 ,,	= 26·8	,,
Carbon residue,	59 ,,	= 1·9	,,
Mineral residue,	16 ,,	= 0·5	,,
Loss (water and gases),	43 ,,	= 1·4	,,

To draw inferences from these figures as to the chemical constitution of india rubber is extremely difficult, if not altogether premature. The formation of these compounds may be accounted for in three ways, and I believe that a careful study of the behaviour of india rubber at temperatures below the point at which dry distillation begins would throw much light upon the mechanism of this splitting-up process. The split might, in the first instance, occur in its totality at a given temperature, about red heat, resulting in the total resolution of the india rubber molecule into isoprene. In this case the terpenes and polyterpenes present in the distillate would have to be looked upon as secondary

[1] Sometimes the boiling point is given as 174·5° C., but this was most likely observed on a still impure product.

[2] It will be observed that this yield of 6 per cent. of isoprene is considerably larger than the yield obtained by BOUCHARDAT (*see* page 22). This is no doubt due to the difference of the conditions under which the dry distillation was carried out.

products—*i.e.*, as polymerisation products of the isoprene. If this is so, it would follow that the yield of isoprene should increase with the rate at which the distillation is carried out, and should also be increased by carrying the distillation products rapidly from the hot retort by means of a current of some inert gas. Or the action of the heat might produce a gradual desintegration of the rubber molecule, accompanied by rearrangement of C_6-chains, into cyclical form and products of the colophene type, the break-down of which might then produce dipentene and isoprene, with the possibility of the formation of the latter being due to the further splitting up of the dipentene ring.

In this case valuable information would be obtained by heating the india rubber for various lengths of time to temperatures somewhat below the point at which actual distillation begins, and examining the changes occurring both physically[1] and chemically. It might be further ascertained whether dipentine, when distilled through red-hot tubes, yields appreciable quantities of isoprene. Or, lastly, the india rubber might, in the first instance, without any change in the size of its molecule, be converted into its corresponding cyclical modification, which then would probably possess considerable stability, and therefore, when breaking up, yield at once all the above characterised products side by side. Although the data furnished by an exhaustive investigation would perhaps scarcely carry us very far towards the solution of the question of the constitution of india rubber, they could not fail to be of the highest scientific and technical value.

As above stated, the behaviour of the various brands of india rubber against temperatures upwards of 100° C. varies considerably as regards the temperature at which the india rubber becomes softened or liquefied. But there appears to be no difference whatever in the products of the break-down of india rubber by heat as it occurs in the process of dry distillation. All brands of india rubber, including Balata and gutta percha, seem to yield the same series of hydrocarbons as Pará itself. It can, however, scarcely be said that this point has been closely studied, and it is quite possible that further research in this direction might reveal differences in these distillation products which would in some degree explain the very marked physical and chemical differences of the various brands of india rubber.

Chemical Behaviour of India Rubber.

The chemical behaviour of india rubber has received less attention than that of any other colloid. The explanation of this fact is no doubt to be found in the circumstance that india rubber is a colloidal hydrocarbon. The absence of reactive carboxyl, hydroxyl, or amido groups deprives the india rubber molecule of those peculiar lines of cleavage, the existence of which determines the nature and constitution of the break-down products

[1] Especially refractometrically.

of complex molecules. And this chemical indifference of india rubber becomes still more accentuated owing to its colloidal state. Indeed, but for the existence of a number of doubly linked carbon atoms in the molecule of india rubber, this substance would in chemical indifference equal, if not exceed, the higher members of the paraffin series. As it is, all the more definite chemical reactions of india rubber are reactions resolving one or more of its double carbon bonds—reactions generally leading to the formation of addition products. Very few only of these have been described, and none of them thoroughly investigated.

Alkalies.—Neither aqueous nor alcoholic solutions of the alkalies appear to have an appreciable action upon india rubber—at any rate, not at temperatures below 100° C. It is, however, stated[1] that on prolonged digestion in these solutions the india rubber becomes sticky and 'greasy.' This change is probably an isomerisation change similar to the one which occurs when india rubber is heated by itself to higher temperatures.

Rather interesting is the observation[2] that on prolonged digestion with *ammonia* the india rubber passes into the state of an emulsion, in appearance closely resembling india rubber milk.

Halogens. *Chlorine.*—WÜRTZ and SCHÜTZENBERGER[3] were the first to observe the action of chlorine upon india rubber, but neither of these authors appears to have recognised the formation of any definite compound. This is, no doubt, due to the fact that they allowed the chlorine to act upon solid rubber, a procedure which might be expected to give unsatisfactory results.

By passing chlorine gas through a solution of india rubber in chloroform, GLADSTONE and HIBBERT succeeded in obtaining a body $C_{10}H_{14}Cl_8$ in the form of a white powder. This formula shows that the reaction taking place was not merely an addition process, but also that substitution of chlorine for hydrogen occurred. Indeed, the authors state that they found it impossible to obtain an addition product $C_{10}H_{16}Cl_6$, as the reaction proceeds so energetically that addition and substitution take place concurrently.

Bromine.—The same observers obtained, by the action of bromine upon india rubber dissolved in chloroform, the products $C_{10}H_{16}Br_4$ and $C_{10}H_{15}Br_5$, although they did not succeed in isolating the former. It was found impossible to obtain the hexabromide $C_{10}H_{16}Br_6$, although the existence of three ethylene bonds in the molecule of india rubber would appear to render such a compound possible. In this relation it may, however, be pointed out that some law of chemical statics seems to prevent the accumulation of iodine and bromine in a molecule, irrespective of the constitution of the latter. Thus the interaction of acetylene and bromine always produces some tribrom-ethylene $CHBr{=}CBr_2$, besides $CHBr_2$:

[1] *Cf.* CHAPEL, *Caoutchouc et Gutta Percha*, 319.
[2] HEINZERLING, *Fabr. d. Kautschuk- und Gutta-Percha-Waaren*, p. 29.
[3] CHAPEL, *loc. cit.*, 322.

$CHBr_2$, which forms the chief product of the reaction. This is exactly analogous to the formation of the above named pentabromide. Iodine only yields a di-iodide with acetylene.

The simplest way to prepare the above named body, polyprene tetrabromide $C_{10}H_{16}Br_4$, is to run bromine in slight excess into a solution of pure india rubber in chloroform, cooling the solution well all the time. Only a very slight amount of hydrobromic acid is evolved during this process. The solution of the tetrabromide thus obtained is transferred to a separating funnel, from which it is run in a very fine jet into alcohol. In order to avoid the tetrabromide separating out in the form of clots, its solution should be very dilute, and a large volume of alcohol should be used for precipitation. The tetrabromide is then obtained in the form of very fine white flakes, which are collected on a filter and washed with warm alcohol until free from every trace of chlorine. The product is then pressed and dried at a temperature not exceeding 40° C. Its composition approximates more and more closely to the formula $C_{10}H_{16}Br_4$, the greater the care taken to free the india rubber from which it was prepared as much as possible from its oxygen.

In the cold, polyprene tetrabromide is fairly easily soluble in chloroform and thiophenol, but quite insoluble in all other solvents tried. It dissolves in aniline, pyridine, and piperidine on moderately heating it in these solvents, but solution always appears to be attended by the loss of more or less hydrobromic acid.

On heating the polyprene tetrabromide to 60° C., it begins to decompose with evolution of hydrobromic acid; a yellow discolouration, which increases in intensity as the decomposition proceeds, becomes at the same time noticeable. At higher temperatures this decomposition proceeds very rapidly, resulting finally in the formation of a very uninviting-looking dark-brown residue, which, however, still contains a more or less considerable quantity of bromine.

The action of boiling alcoholic caustic soda upon the tetrabromide is surprisingly slight, but sodium ethylate has a more pronounced effect, especially at temperatures ranging from 100° C. upwards.

0·624 grms. of $C_{10}H_{16}Br_4$ were heated with sodium ethylate to 100° C. in a sealed tube for 6 hours:

Solid substance recovered	: 0·3623 grms.	= 58·06 per cent.	
Br in recovered portion	: 0·1134 ,,	= 18·28 ,,	[1]
Br in solution	: 0·3210 ,,	= 51·44 ,,	

0·6154 grms. of $C_{10}H_{16}Br_4$ were heated with sodium ethylate to 120° C. for 10 hours:

Solid substance recovered	: 0·3438 grms.	= 55·87 per cent.	
Br in recovered portion	: 0·0823 ,,	= 13·38 ,,	[1]
Br in solution	: 0·3478 ,,	= 56·51 ,,	

[1] The amount of Br is calculated upon the weight of the original substance employed, and not upon the weight of recovered solid substance.

Attention must be called to the fact that the weight of substance recovered plus the weight of bromine in solution in both experiments is considerably in excess of the weight of tetrabromide used. This must be accepted as pointing to the fact that the removal of the bromine is a substitution process, probably of ethoxyl groups for bromine.

Against acid and oxidising reagents the tetrabromide exhibits considerable indifference. Concentrated nitric and sulphuric acid affect it very slowly. Chromic acid, or mixtures of chromic and sulphuric acid, are without any perceptible action, even at 100° C.

Very remarkable is the reaction which takes place on heating the tetrabromide with phenol. The operation is best conducted on the water-bath by adding the tetrabromide to the melted phenol. Already at 60° C. a rapid change of colour is noticeable, the tetrabromide assuming first a dull slate colour which rapidly darkens to a blackish-brown. The mass at the same time becomes gummy and begins to form a brownish-purple solution with the phenol. At this stage a steady evolution of hydrobromic acid gas commences. As the reaction proceeds, the mass grows thinner until, after about thirty minutes' heating, a thin purple-coloured solution is obtained. This solution is allowed to cool, and, after dilution with twice its volume of ether, it is filtered. If the operation has been properly conducted, there should remain no insoluble residue on the filter. The filtrate is then distilled on the water-bath until no more ether passes over, and the residual solution is poured into a sufficient quantity of a 6 per cent. solution of caustic soda, in order to dissolve all the phenol present. A dark-brown solution is obtained, which is heated until all the residual ether is driven off. Acetic acid is then slowly added until a permanent, greyish-brown, and flocculent precipitate has been formed. This is separated from the phenol solution by filtration, and, without previous washing, again suspended in warm water and acidulated with acetic acid. The suspended precipitate changes its colour into a more or less pronounced brown, much resembling the colour of ferric hydroxide. It is heated to boiling, filtered and washed free from acid. When dry, it forms an ochre-coloured mass, easily reducible to an impalpable powder.

This substance is readily soluble in aqueous and alcoholic caustic soda, alcohol, acetone, ethyl ether, ethyl acetate ; insoluble in benzene, chloroform, carbon bisulphide, and petroleum ether. Its analysis gave the following figures :—

0·1622 grm. substance, . . .	0·4785 grm. CO_2, 0·1184 grm. H_2O.
Calculated for $C_{34}H_{36}O_4$, . . .	C 80·16, H 7·14.
Found, ...	C 80·15, H 7·42.

The analysis agrees very well with the figures calculated for a body $C_{10}H_{16}(O.C_6H_5)_4$, tetroxyphenyl-polyprene, and its formation therefore would appear to be due to the very remarkable reaction

$$C_{10}H_{16}Br_4 + 4C_6H_5OH = C_{10}H_{16}(C.OH_5)_4 + 4HBr.$$

hydroxide. The thorough washing of these precipitates is extremely tedious. After drying, they form very hard, almost black, resinous masses. I refrain from quoting analyses of these bodies, but may mention incidentally that, on drying, these colloidal products suffer very extensive dehydration.

I am continuing the investigation of these curious bodies, which, I believe, will furnish excellent material for the prosecution of the enquiry into the nature and constitution of india rubber. The reaction to which we owe their formation is by no means confined to phenol. The cresols carvacrol, thymol, as well as the naphthols, react in quite an analogous manner. Resorcinol, under the conditions above stated, reacts most energetically, forming an eosin-coloured mass. Pyrocatechol and hydroquinone react much more slowly. Of substituted phenols the action of the three chlorophenols and of the three nitrophenols was examined. The first named yield chlorinated reaction products; the last named appear to complicate the reaction by oxidation. Thiophenol acts in an entirely different manner, by simply eliminating the bromine of the tetrabromide as hydrobromic acid. Phenol-ethers, such as anisol or phenetol, do not react at all. This is almost conclusive evidence that it is the hydroxyl hydrogen of the phenol which forms the point of attack in the reaction in question, and this fact is at the same time the reason why, in the above formulæ, the oxygen appears as ether oxygen, and not as hydroxyl oxygen.

Iodine.—ADRIANI [1] states that the action of iodine on the globules of the latex is more marked than that of bromine, but he does not appear to have investigated the nature of this action. On the other hand, however, GLADSTONE and HIBBERT found iodine to have little or no action upon india rubber dissolved in chloroform.

My own observations on this subject tend to show that iodine does indeed act upon india rubber dissolved in chloroform. A 3 per cent. solution was mixed with a large excess of iodine (3 mols. of I to 1 mol. of india rubber) dissolved in chloroform. After two days' standing, the mixture had become gelatinous. It was thoroughly stirred and transferred into absolute alcohol. An insoluble precipitate formed, which was completely freed from iodine by washing with warm alcohol. In this manner a bright straw-coloured product was obtained in the form of a fine powder, which was found to be absolutely insoluble in all ordinary solvents. This preparation on analysis gave the following figures:—

0·5470 grms. gave by CARIUS' method 0·7273 grms. AgI.
0·2008 grms. gave 0·1689 grms. CO_2 and 0·0560 grms. H_2O.

		Calculated for $(C_{10}H_{16}I_3)_x$.
Carbon, . . .	22·35 per cent.	23·21
Hydrogen, . .	3·07 ,,	3·09
Iodine, . . .	72·03 ,,	73·69
	97·45	

The original sample of india rubber from which this preparation was

[1] *Chem. News*, 2, 278.

made contained 3·94 per cent. of oxygen, which is obviously responsible for the deficiency in the above analysis. Nevertheless, these figures agree fairly with the ratio $C_{10}H_{16}I_8$. Of course an addition product of this formula is not possible, and we must therefore assume that this tri-iodide has been formed by a process analogous to that which leads to the formation of the pentabromide,

$$C_{10}H_{16}I_4 = C_{10}H_{15}I_3 + HI.$$

The difference of one atom of hydrogen is so small as to fall within the limits of the experimental error. The splitting off of hydroiodic acid in this manner is, however, perhaps not very probable, and the difficulty of explaining the composition of the above addition product might very likely be met by the fact that india rubber is not $C_{10}H_{16}$ but $(C_{10}H_{16})_n$, so that if n is an even number, the number of iodine atoms in our substitution product necessarily becomes even too.

This iodide is a far less stable substance than the bromide. Its colour changes to a dull brown on prolonged exposure to light, but this change of colour does not seem to be accompanied by loss of iodine. At 80° C. the compound undergoes slow but complete decomposition. A dark-brown resinous body remains behind, most likely an oxidation product of india rubber. The iodide was found to be insoluble in all solvents.

Action of Acids. *Hydrochloric Acid.*—Although the destructive action of hydrochloric acid gas upon india rubber stoppers and tubing must have been observed by thousands of chemists, the cause of this action has never been investigated until quite recently by myself.

The action of hydrochloric acid gas upon india rubber dissolved in chloroform differs materially according to whether moisture be present or not. In the latter case I have not been able to obtain any definite result. The evidence at hand appears to show that a product $C_{10}H_{16}.HCl$—polyprene hydrochloride—is formed, but I have never been able to obtain a product containing the requisite amount of chlorine.[1] Moreover, all preparations obtained under these conditions form very sticky masses which are very difficult to handle. Once precipitated they are very insoluble, and therefore practically impossible to purify.

If the hydrochloric acid gas is passed in the undried state into the india rubber solution at ordinary temperature, the result is different. The absorption proceeds at first fairly rapidly, but gradually becomes slower, and it is therefore necessary to allow the gas to pass through the solution for a whole day. At the end of this time the solution has perceptibly darkened in colour, but appears otherwise unchanged. On pouring this solution slowly into absolute alcohol, it is precipitated as a mass of whitish clots which are still sensibly elastic to the touch. On standing for a short time under alcohol, these clots become hard and brittle, often

[1] The products obtained under various conditions of temperature were found to contain from 11 to 18 per cent. of Cl. The body $C_{10}H_{17}Cl$ would contain 20·22 per cent. of Cl.

breaking up spontaneously into a mass of small irregularly-shaped fragments. This product is washed free from acid with warm alcohol, and dried in a desiccator. It forms a perfectly white, easily friable substance, which is readily soluble in chloroform, but insoluble in alcohol, ether, acetone, benzene, and carbon bisulphide. On gently warming it with organic bases such as aniline, pyridine, or piperidine, it dissolves gradually, but this solution appears to be accompanied by loss of hydrochloric acid. The analysis of this compound led to the following figures:—

0·3837 grms. gave by CARIUS' method 0·5223 grms. AgCl.
0·2188 grms. gave 0·4588 grms. CO_2 and 0·1615 grms. H_2O.

		Calculated for $C_{10}H_{18}Cl_2$.
C, . . .	57·12 per cent.	57·41 per cent.
H, . . .	8·13 ,,	8·62 ,,
Cl, . . .	33·67 ,,	33·97 ,,

These figures agree well with those of a polyprene dihydrochloride. The india rubber from which the specimen analysed was prepared contained 2·10 per cent. of oxygen. This hydrochloride is rather difficult to prepare, as it gives off part of its hydrochloric acid very readily, so that in many preparations the percentage of chlorine fell as low as 31 per cent. On the other hand, it is worth mentioning that as soon as the decomposition of the dihydrochloride has reached a point that the amount of residual chlorine is about 18 per cent., even a very considerable increase of temperature will cause only a very insignificant further reduction in the percentage of chlorine. Seeing that 18 per cent. of Cl comes very near the amount of chlorine required for polyprene monohydrochloride, we may perhaps infer that this forms the chief product of the decomposition of the dihydrochloride at temperatures not exceeding 100° C., and that, compared with the latter, it is a rather stable body.

Hydrobromic Acid.—The action of hydrobromic acid upon india rubber is much the same as that of hydrochloric acid, although rather slower. It has been found impossible to prepare a hydrobromide corresponding to the above described dihydrochloride. On passing hydrobromic acid gas into a solution of india rubber in chloroform, and subsequently running this solution into alcohol, a product is obtained which in appearance greatly resembles the dihydrochloride, but already on washing with alcohol it begins to lose hydrobromic acid. I have never succeeded in preparing a compound with more than 21 per cent. of bromine, and the appearance of all preparations I obtained clearly indicated their heterogeneous nature.

Hydriodic Acid.—This acid seems to have no action upon india rubber, or, if formation of a hydro-iodide does take place, this compound must be extremely unstable. According to BERTHELOT,[1] treatment of india rubber with hydriodic acid at 280° C. results in the formation of viscous hydro-

carbons of the paraffin series, boiling without decomposition above 350° C. This statement requires confirmation.

Sulphuric Acid.—The concentrated acid acts very energetically upon india rubber, charring and oxidising it. Nothing definite is, however, known respecting the ultimate products of this destructive action. The action of dilute sulphuric acid has never been investigated.

Nitric Acid.—Strong nitric acid attacks india rubber very vigorously, forming at first a yellow body which is subsequently decomposed into nitrogen, carbonic acid, oxalic acid, and a substance of the character of a fat.[1] On prolonged boiling, this latter body is dissolved and converted into camphresic acid, which was shown by KACHLER[2] to be a mixture of camphoric and camphoronic acid.

Nitrous Acid.—In treating a dilute solution of india rubber with nitrous acid, produced by very slowly running concentrated sulphuric acid into a 20 per cent. solution of sodium nitrite, an amorphous yellow body is formed, insoluble, or very little soluble, in most of the commonly employed solvents, but fairly soluble in dimethyl oxalate. The composition of this body, as obtained in different preparations, varies very greatly, but by passing the nitrous acid gas, prepared as described above, through a series of drying tubes charged with phosphoric anhydride, and by using absolutely dry india rubber dissolved in benzene, which has been freshly distilled over metallic sodium, a product is obtained showing the following composition :—

	C 55·5,	H 7·0,	N 13·1.
Calculated for $C_{10}H_{16}N_2O_3$:	C 56·6,	H 7·5,	N 13·2.

The product of the reaction is evidently polyprene nitrosite. The full investigation of this highly interesting body is not yet concluded.

Nitrogen Dioxide.—In treating a solution of one part of india rubber in a hundred parts of absolutely dry benzene with nitrogen dioxide, a considerable rise of temperature takes place, and the whole of the india rubber present separates out in the form of a coherent amorphous mass. The nitrogen dioxide is most conveniently produced by heating well dried lead nitrate in a retort. The gas evolved must be dried by passing it through a series of tubes containing phosphoric anhydride.

The above described operation being completed, the benzene, which will be found to contain mere traces only of solid matter, is poured off the product of the reaction. The latter forms a very friable mass, which, after washing with alcohol, is obtained as a dark-yellow powder. This product is, however, not yet pure. It dissolves in acetone with the greatest ease, forming a deep sherry-coloured solution containing in suspension a small quantity of an insoluble substance. This is filtered off, and the perfectly clear solution run into water. The very fine precipitate thus obtained is collected on a filter, washed with water, pressed, and dried,

[1] SCHWANERT, *Ann.*, 128, p. 123.

[2] *Ann.*, 191, p. 143.

when it is obtained as a straw-coloured impalpable powder, which, on analysis, gave the following figures:—

C 52·5, H 7·1, N 12·3.
Calculated for $C_{10}H_{16}N_2O_4$: C 52·6, H 7·0, N 12·7.

Whether this body represents a dinitro-polyprene $C_{10}H_{16}(NO_2)_2$, or a nitroso-nitrate (nitrosate) similar in constitution to WALLACH'S[1] amylene-nitrosate,

$$C_5H_{10}\begin{cases} NO \\ O.NO_2 \end{cases}$$

further investigation will have to show.

The product purified as above described is insoluble, or only very slightly soluble, in ethyl alcohol, methyl alcohol, ether, chloroform, and carbon bisulphide. It dissolves almost instantly in acetone, and is also fairly soluble in ethyl acetate, ethyl formate, dimethyl oxalate, epichlorhydrine, and nitrobenzene. Ammonia dissolves it very readily even in the cold, but it is almost insoluble in either aqueous or alcoholic soda.

This product, as already mentioned, is insoluble in methyl alcohol, but, on adding to the latter a few drops of very concentrated caustic soda, or, better still, a small quantity of sodium methylate, solution takes place instantly. Curiously enough, ethyl alcohol cannot be used in this reaction instead of methyl alcohol. The action of the alkali upon the polyprene derivative appears to be the same in both cases, but the product of the reaction is soluble only in methyl alcohol, and not in ethyl alcohol. Indeed, on adding to its solution in methyl alcohol an equal volume of ethyl alcohol, a flocculent precipitate is at once formed. The investigation of these bodies is still proceeding.

Nitrosyl Chloride.—On treating a solution of 13·6 grms. of polyprene in 300 c.c. of benzene with 12 grms. of amyl nitrite and 8 grms. of acetyl chloride, a reaction takes place, resulting in the formation of a very stiff jelly. After about 20 minutes' standing gas bubbles appear in the jelly, which rapidly grow in size and number. In the course of a few hours the jelly is reconverted into a solution distinctly thinner than the original rubber solution. On precipitating this solution, a clot of a substance is obtained, which, after purification, by again dissolving and precipitating it, was found to be apparently unaltered polyprene containing traces only of chlorine and nitrogen. A polyprene nitrosyl chloride could in no way be obtained.

Oxygen.—The action of oxidising agents, such as chromic acid, potassium permanganate, persulphates, and percarbonates, upon india rubber has never been systematically investigated. Ethereal solutions of hydrogen peroxide are stated to convert india rubber into products soluble in alcohol, but I have never been able to confirm this result.

The liability of both crude and vulcanised india rubber to deteriorate under the influence of atmospheric oxygen has been known for some con-

[1] *Ann. Chem.*, 241, 288 [1887].

siderable time, and was investigated by SPILLER,[1] who isolated a product soluble in alcohol and chloroform, melting below 100°, and which possessed the following percentage composition:—

C,	. . .	64·00 per cent.
H,	. . .	8·46 ,,
O,	. . .	27·54 ,,

It is perhaps worth pointing out that this composition fairly closely corresponds with $C_{30}H_{48}O_{10}$. This may be accidental, but as this body still shows the ratio $C_{10} : H_{16}$, this formula, at any rate, appears to prove that this oxidation process is purely an addition process.

SPILLER'S observations were made on a thin film of manufactured but unvulcanised india rubber. Articles of this description are, under normal conditions, only very slowly affected in this manner, owing to their non-porosity and smoothness of surface. Crude india rubber, particularly in the state of the highly porous and reticulated sheets in which it leaves the washing-machine for the drying-room, is apt to suffer considerably from oxidation during the drying process.

The Vulcanisation of India Rubber.

Historical Introduction.—From a technical point of view, the action of sulphur and of sulphur monochloride upon india rubber is of fundamental importance. It may well be said that to the action of these two compounds the india rubber industry of to-day chiefly owes its existence and extent.

1. *Vulcanisation with Sulphur.*—In 1832 LÜDERSDORF made the observation that sulphur removes the natural stickiness of india rubber, and at about the same time an American, HAYWARD, employed flowers of sulphur to counteract this stickiness of india rubber sheets. It was, however, unquestionably NELSON GOODYEAR who, in 1839, first definitely established the fact that the treatment of india rubber with sulphur at high temperatures has the effect of maintaining the elastic properties constant within a comparatively very wide range of temperatures, and who subsequently also discovered the manufacture of ebonite, the final product of the action of sulphur upon india rubber. In England HANCOCK appears to have independently made the discovery of the vulcanising action of sulphur, but as, according to his own statement,[2] he had seen samples vulcanised by Goodyear, the priority of this invention clearly belongs to the latter. HANCOCK'S narrative of his countless attempts to produce such a product, and the manner in which he finally succeeded, is so fascinating, that an extract of it from his above quoted book, which is by no means readily obtainable, may be acceptable.

"Some time in the early part of the autumn of 1842, Mr. Brockedon

[1] *Journ. prakt. Chem.*, 94, 502.

[2] HANCOCK, *Personal Narrative of the Origin and Progress of the Caoutchouc or India Rubber Manufacture in England*, London, 1857, p. 94.

showed me some small bits of rubber that he told me had been brought by a person from America, who represented himself as the agent of the inventor: it was said that they would not stiffen by cold, and were not much affected by solvents, heat, or oils. Mr. Brockedon told me that the mode of manufacturing this rubber was a secret, and that the agent who had shown them to him, declared himself totally ignorant of it; all he knew was, that it had been done by some new solvent which was very cheap in America, and that he wished to find parties who would purchase the secret in this country, and asked Mr. Brockedon to give him any introduction he could to the trade. Mr. Brockedon gave him the names of Mackintosh & Co., and the representatives of the Caoutchouc Company (and I think at least one other), with whom the party also left specimens. Mackintosh & Co. told the agent that, as he could give no information, they could not judge of the merits of the invention, as it might be easy to make these small specimens, whilst difficulties might be found in its application upon a large scale; nor could they judge whether their present appliances, which had been very costly, would be suitable for this manufacture, or whether any modification of their present plant would answer, or whether the modes were so altogether new as to require a fresh outlay. Under these circumstances, as they could not act in the dark, they recommended the taking out of a patent, when a clear comprehension of the whole could be obtained, and the invention openly dealt with according to its merits. This course was approved of, and the agent said he would immediately advise his principal to take out a patent.

"Mr. Brockedon cut, from two of the small pieces which had been given him, two very diminutive bits, and gave them to me; one bit was about one and a half or two inches long, and one inch and a quarter wide, and perhaps the twentieth of an inch thick. This bit, on the exterior, was of a dirty yellowish-grey colour, and a little dusty powder upon it; when cut across, the cut edge appeared of a dark colour. The other bit was of a dark reddish-brown colour throughout, with a clean surface without any dusty appearance. The first named had a slight smell of sulphur, and I thought that a little sulphurous powder had been rubbed on to mislead. On stretching them out thin, I observed they were both quite opaque. I found they were, as stated, not affected by cold.

"Finding now that this object had been somehow or other effected, and therefore demonstrated to be practicable, and as it was my particular department to keep up the quality of our manufactures, and to maintain our standing and the position our goods had attained, I set to work in earnest, resolved, if possible, not to be outdone by any. As I advanced, I spent all my spare time to attain the two objects I had in view.

"I succeeded in producing beautiful drab- and tan-coloured surfaces, perfectly inadhesive, by combining silicate of magnesia, and compounds of this silicate, with fuller's earth, whiting, ochre, and other earths, in all of which the silicate of magnesia formed the foundation and predominated.

For a dark colour I employed asphalt, both the natural mineral kinds as well as that obtained by boiling down coal-tar to the state of asphalt. With this asphalt I also sometimes combined plumbago, and by these means produced an unadhesive black surface. Since that time, a taste for a more glossy article prevailing, varnishes have been added. In carrying out these improvements, no new machinery was needed, the rubber and compounds being made, and the straining and spreading effected, by the means before mentioned.

"During my progress with these experiments, I gave attention also to my other object, and having nearly brought the former to a close, I could give to the latter more special attention. The little bits given me by Mr. Brockedon certainly showed me for the first time that the desirable change in the condition of rubber of not stiffening by cold had been attained, but they afforded no clue to the mode by which it had been brought about.

"As the knowledge of this improvement in the qualities of rubber soon spread abroad, several persons began to make experiments in order to discover means to effect the same; but as there were very few who at that time had any considerable experience in the treatment of rubber beyond the ordinary applications for waterproofing purposes and the construction of pneumatic articles, they were not very likely to succeed in an attempt which required, besides an experimental knowledge of the subject, unwearied application and the closest observation of the effects of every new addition to the compounds, and of the proportions indicative of improved results—nor were high temperatures employed by such persons. Mr. A. Parkes, for instance, was not much acquainted with the rubber manufacture, and therefore, after he had seen my specification, and the change that had been effected by sulphur and heat, went immediately to work as a chemist, and tried the effect of the whole round of sulphurous combinations with the rubber, and for a time gave up the pursuit; but being urged to continue his experiments, he at length succeeded, by purely chemical means, in effecting a change in rubber very closely resembling vulcanisation.

"It is a singular fact that although sulphur had long been compounded with rubber by myself in this country, and in America by others, yet that its true value for producing such a result had never been even dreamt of by any of us. I made no analysis of these little bits, nor did I procure, either directly or indirectly, any analysis of them. In making my experiments, I depended entirely and solely on my own exertions, having some confidence in an experience of upwards of twenty years of unceasing application to the manipulation with my own hands of the substance I was dealing with; and it having been shown that rubber could be so made as not to stiffen by cold, I devoted myself to the discovery, if possible, of some mode by which this property could be imparted; and I considered the small specimens given to me simply as a proof that it was practicable. It had been my constant practice to make my experiments alone in my private laboratory at Stoke Newington, into which, on these occasions, no

person entered but myself. I consequently lighted my own fires, and did all the labour myself; and having constantly to attend to the general business in London, and to answer innumerable enquiries, both verbally and by letter, besides attending consultations with parties taking out patents, or others requiring information in the application of our materials to their different purposes, I was obliged in a great measure to pursue my experiments after the hours of business, and was frequently employed till midnight in these labours. I think it necessary to mention this, because it has been alleged that nothing could have been less difficult than such a discovery, and that anyone acquainted with the substance might have accomplished it with great ease. After a discovery is once made, it is generally said to be easy of attainment; anybody might have done it, the thing was so simple. According to Milton, an idea of this kind occurred to some as far back as the council in Pandemonium:—

> 'The invention all admired; and each how he
> To be th' inventor missed, so easy it seem'd,
> Once found, which yet unfound most would have thought
> Impossible.'

"But to resume, I knew nothing more of the composition of the small specimens given me by Mr. Brockedon than what I or any other person might know by sight and smell. In such a pursuit I was obliged to grope a good deal in the dark; for although my former experience, such as heat, masticating, rolling, and the use of solvents, served as landmarks, still my experiments could only be made pretty much at random, not at all knowing what the result of any of them might be. I remember that I had from the first a strong impression that the rubber underwent the change either when in a state of solution or when greatly softened by heat, and these two points I kept pretty much in view. I compounded with the rubber in one or other of these conditions an almost endless round of matters of all kinds.

"I treated these with the rubber separately and in innumerable combinations. In some of them I included sulphur, and employed heat in almost every case without regarding what degree of heat I used. I have, in an early part of my narrative, stated how useful I found it to employ high temperatures, and attribute my final success in my present pursuit to the habit I had acquired in its use, particularly when I thought it necessary to reduce the rubber to the softest or most plastic state without solvents. When making the compounds with solvents, I first dissolved the rubber, either making the solution of a thin consistence, or of the consistence of dough, and then mixed or worked up the other matters with it. When I wished to expedite their drying, I sometimes laid them on a small metal plate heated over a chamber lamp, or larger plates heated by the fire, and at other times I submitted them to the heat of an oven. As before mentioned, I frequently employed sulphur in the compounds, but they were not at all improved by it, not having yet by any chance used heat

sufficiently high when drying them to produce the change; or, if the heat was sufficient, which it most likely sometimes was, the compound became dry in too short a period to affect it (as I removed the pieces as soon as they were dry) in any way to attract my observation, having nothing to guide me in the object in view. I therefore for a time relinquished the use of sulphur in most of the compounds as useless, and pushed on with other matters, still feeling a conviction, as I think most would naturally have done, that the rubber must necessarily undergo the change in its constitution whilst either very soft and plastic or in a state of solution. However, after trying an endless round of mixtures in this way, with and without heat, I still failed of success.

"Whilst looking over some of my former experimental scraps, I saw in some of those containing sulphur, variations I could not at the time account for: some portions were different to others in the same specimen, which for the present I could not comprehend, although I well knew afterwards. I resolved now to take another course; I dissolved sulphur in oil of turpentine, and finding the solution proceed slowly, I raised the temperature of the turpentine to the boiling point (316°), and then it took up the sulphur freely. Rubber dissolved in this solution was good in some respects, but produced a weak material, and did not come up to my wishes.

"I spent all my spare time for months with these experiments; my habit was to despatch them quickly, making them very small in bulk, throwing aside some thousands of trial scraps, and selecting and keeping for inspection any that appeared promising. During the winter months I generally found the weather cold enough to test my scraps, but as the spring and summer came on, I employed ice, purchased from an ice-cart which passed my gate every morning, and many an earnest and careful examination have I made in a morning of the scraps in the ice.

"My experiments now had become very interesting; I had certainly produced in some of my scraps, or portions of some of them, that condition of rubber which I afterwards called the 'change.'

"I cannot, of course, now say in which scrap or at what particular moment I struck out the first spark of the 'change,' because I had a great number of scraps under my hand at one time, and I also found that when exposed even to ice, the stiffening effect of cold was not always immediately apparent; and I was thus, during my comparative ignorance of the nature of my discovery, frequently misled and disappointed from two causes: first, what it was in the successful compounds that produced the effect; and secondly, I was ignorant of the importance of the degrees of temperature employed, as well as of the like importance of the period to which any specific compound required to be submitted to heat.

"These points could be ascertained with exactness only by time and vigilant watching, and this I began immediately to set about; and as the law allows a patentee six months to work out his discoveries before he is

called upon to enrol his specification, I applied for and obtained a patent for my inventions, which passed the great seal on the 21st November 1843.

"I found that, when submitting the compounds containing sulphur to heat, it was necessary, after ascertaining the temperature that suited any compound, to find also the period of exposure to the heat that produced the best result. Until I noticed the necessity for this particularity, I was often sadly perplexed, as the same compounds exposed to the same temperature were sometimes good and sometimes bad in practice: the variation is from one to six or seven hours, or more. All the way through these experiments for producing the 'change,' I had no other guide, of course, than to watch for any promising appearance in any of the scraps, and to improve upon them; but I now know I was frequently thwarted by my want of information as to what cause the different appearances were due, and particularly in regard to the temperature I employed, which was somewhat at random, knowing how freely I could use it within certain limits without injury.

"A thought now occurred to me that in the end proved extremely valuable. Revolving in my mind some of the effects produced by the high degrees of heat I had employed in making solutions of sulphur and rubber, as before stated, in oil of turpentine, it occurred to me that as the melting point of sulphur was only about 240°, which I knew would not be injurious to the rubber, it would be well to see what would ensue on immersing a slip of sheet rubber in sulphur at the lowest melting point. I accordingly melted some sulphur in an iron vessel and immersed in it some slips of cut sheet rubber about half an inch wide and about one-sixteenth of an inch thick. After they had remained some time I examined them, and found the surface had assumed a yellowish-tan colour. I immersed them again; and on withdrawing them the second time, I cut one of them across with a wet knife, and found that the rubber was tinged of this tan colour to a considerable depth. I immersed them again; and on the third examination I found the tan colour had quite penetrated through the slip. This was strong evidence that the rubber had freely absorbed the sulphur, and I fully expected to find that these slips were now 'changed,' but in this I was greatly disappointed, for, on applying the tests, I found that not the least 'changing' effect had been produced. I now replaced them and raised the temperature of the sulphur, and allowed them to remain a considerable time; and on withdrawing one of them the fourth time, I found to my great satisfaction that it was perfectly 'changed,' retaining the same tan colour throughout. The other slips remained in the sulphur whilst this examination was going on, and on withdrawing them, I found the lower and nearest the fire turning black and becoming hard and horny, thus at once and indubitably opening to me the true source and process of producing the 'change' in all its pure and pristine simplicity."

The action of sulphur upon india rubber depends upon a great number of factors, the most important of which is heat. Whether the action be induced by immersing the india rubber into molten sulphur, or by ex-

posing mixtures of india rubber and sulphur to temperatures above the melting point of sulphur (114° C.), no marked action takes place until the temperature has passed 120° C. Even then, what reaction does take place proceeds with extreme slowness. For practical purposes the temperature employed ranges from 125 to 360° C.

The amount of sulphur employed in practice varies very greatly, from 4 up to 50 per cent.; but the amount of sulphur fixed by the india rubber very rarely exceeds 3 per cent., and is generally less. It is therefore obvious that free sulphur in various proportions always forms a constituent of ordinary vulcanised india rubber goods.

The vulcanisation process is considerably accelerated, and in several respects distinctly facilitated, by the presence of sulphur carriers. In this respect antimony pentasulphide, arsenic pentasulphide, arsenic trisulphide (orpiment), and arsenic disulphide (realgar) prove most effective, and, in a lesser degree, lead thiosulphate, lead sulphide, zinc sulphide, lead oxide (litharge), and lead carbonate (white lead).

It is, however, not only by means of free sulphur that the vulcanisation of india rubber can be effected. GÉRARD showed that this can also be done by heating the india rubber with solutions of the alkaline polysulphides. Indeed, this process renders it possible to effect vulcanisation at temperatures very little above the boiling point of water.

The nature of the vulcanisation process is still very little understood, most of the writers expressing themselves very guardedly upon this point, and attributing vulcanisation to 'absorption' of sulphur. BURGHARDT[1] suggests that vulcanisation consists "in the alteration of the caoutchouc resin through the production in it of a 'sulpho-compound,' a certain amount of hydrogen in the caoutchouc being replaced by sulphur." BURGHARDT evidently overlooks the fact that this assumption would imply the formation of 34 parts of hydrogen sulphide for every 32 parts of sulphur combining with the india rubber. If this view was correct, the amount of hydrogen sulphide produced by an india rubber factory vulcanising only 5 cwt. of india rubber per day would amount to considerably over 100 cubic feet per day. There would be, to say the least of it, strong evidence of the evolution of such a volume of this obnoxious gas in the vulcanising rooms, which, under normal conditions and circumstances, is never the case. Numerous experiments I conducted to detect the evolution of this gas in the vulcanising process under laboratory conditions failed to disclose the formation of even traces of hydrogen sulphide.

Very likely BURGHARDT'S view was founded upon a statement by PAYEN on this point, which is to the following effect:—"With the beginning of this reaction, and during the whole of the time it is in progress—that is, at a temperature of from 135 to 145° C.—combination of the sulphur with a small quantity of the hydrogen of the organic substance is going on, resulting in the continuous formation of hydrogen sulphide, of which sulphur can

[1] *Thorpe's Dict. of Appl. Chem.*, vol. ii. p. 312.

absorb nearly its own volume. A curious phenomenon results from this fact *if the vulcanisation is carried out in a bath of melted sulphur*: as soon as, on completion of the operation, the temperature of the bath is allowed to fall, the crystallising sulphur liberates the hydrogen sulphide, and the evolving gas causes the semi-fluid mass of sulphur to rise."

This statement is not very conclusive concerning the point in question, and assuming that PAYEN employed in his experiments india rubber which had not first been freed from all resinous and oily matters, the evolution of hydrogen sulphide in small quantities would thereby be explained. However, PAYEN'S experiments led him to consider the vulcanising process as a substitution of sulphur for hydrogen.

HEINZERLING expresses himself as follows on the vulcanising question:— "It is not known with certainty whether the chemical union of sulphur with india rubber is an addition or a substitution process. That chemical combination does take place seems to follow with necessity from the fact that, whereas before vulcanisation both india rubber and sulphur are soluble in carbon bisulphide, they are rendered completely insoluble by this process."

DONATH'S views upon this subject are interesting. He seems to consider the vulcanising process, not as a purely chemical phenomenon expressible in definite terms of molecular interaction, but as a phenomenon of molecular aggregation in indefinite proportions, and in many respects comparable to metallic alloys. Against the assumption of definite compounds of sulphur and india rubber, he objects that vulcanisation can be carried out by means of metallic sulphides as readily as with free sulphur, which fact would necessitate the assumption that the sulphides of antimony, mercury, and lead give up their sulphur to the india rubber.

TH. SEELIGMANN[1] assumes "that the phenomenon which is understood by the name of vulcanisation is only the first of a series of successive transformations occurring at definite temperatures and in the presence of excess of sulphur in the hydrocarbons which constitute india rubber. The terminal stage of this transformation series is reached with ebonite, which, if we adopt the views of C. O. WEBER, would represent one or more double atoms of polyprene linked together by one or more atoms of sulphur.

"To us vulcanisation appears simply as an operation by which, at the most opportune moment and at a certain stage, a chemical reaction is arrested, the completion of which would lead to a vastly different product than the one it is desired to obtain."

The only element of progress in SEELIGMANN'S view, as it appears to me, is his somewhat timid adoption of the view of the nature of vulcanisation first stated by me some years ago.[2] For a satisfactory theory of vulcanisation this is scarcely sufficient.

[1] TH. SEELIGMANN, *Le Caoutchouc et la Gutta Percha*, Paris, 1896, p. 178.
[2] *Soc. Chem. Ind.*

SEELIGMANN believes that an argument in favour of his views is furnished by an experiment by PAYEN, which I quote in full:—

"Ether and carbon bisulphide, on prolonged standing with vulcanised india rubber, dissolve about 4 to 5 per cent., which can be isolated and separated from free sulphur by evaporation and re-solution in ether. The rubber obtained from the ethereal solution yields to absolute alcohol from 1 to 1·5 per cent. of fatty matter.

"The india rubber thus extracted can be separated into two parts, one of which is very ductile and soluble in benzene, from which it can be obtained by evaporation, while the other part is tougher, less elastic, and insoluble. These two parts are derived from the inner parts of the vulcanised rubber where the compound is less resistant and poorer in sulphur than the parts near the surface.

"After its vulcanisation there exist in the india rubber still two parts possessing different degrees of cohesion and solubility. This becomes noticeable on keeping a piece of vulcanised rubber tape immersed during two months in a mixture of carbon bisulphide and absolute alcohol (10 : 1). The solution thus obtained is evaporated to dryness, the free sulphur removed by treatment with caustic soda, and we obtain then the less aggregated part of the organic substance (our 'adhesive' hydrocarbon transformed by sulphuration) possessing little strength, yellowish in colour, and translucent. The insoluble part of the tape is found to have preserved its form, but to have turned brown and less transparent (our more sinewy[1] hydrocarbon undiluted by the adhesive and soluble part). These constituents, omitting the fatty matter, were obtained in the following proportions:—

Insoluble, sinewy portion, ...	65 per cent.
Soluble, adhesive portion, ...	25 ,,
Free sulphur, ...	10 ,, "

I have no reason to doubt that PAYEN effected a separation of vulcanised rubber into a soluble and an insoluble part in the above proportions, but I emphatically deny that this separation bears out in the least the important conclusions PAYEN based upon it. The extent to which the fact of the existence of an insoluble constituent in india rubber has inspired the imagination of our French colleagues is truly astonishing. But even more so is the uncritical manner in which the amount of this insoluble matter in india rubber has been exaggerated to about ten times its real value, assuming at the same time for this insoluble part identity of elementary composition with that of the soluble part, and all this in the absence of any reliable analytical data of any sort.

PAYEN'S above described experiment, and its entirely erroneous interpretation, prove nothing for or againt SEELIGMANN'S before stated views regarding the nature of vulcanisation. They appear to me merely as an attempt to demonstrate the persistence in the india rubber even after

vulcanisation of its 'sinewy' and of its insoluble, as well as of its adhesive and soluble, constituents. We have, however, seen[1] that the insoluble part of india rubber (Pará) forms a very insignificant portion only of the whole, and we have also disposed of the current assumption that the composition of this insoluble part is identical with that of the rest of the india rubber.

I have attempted to repeat PAYEN's above described experiment in order to make an exhaustive examination by analysis of the products of this separation. A specimen of Pará rubber vulcanised with 10 per cent. of sulphur at 135° C. during two hours was employed. This specimen contained after vulcanisation 3·98 per cent. of combined, and 5·96 per cent. of free, sulphur. It was cut into very fine threads, which were during three months kept submerged in PAYEN's mixture of carbon bisulphide and alcohol (10 : 1). At the end of this time the threads, although much distended and swelled, showed not the slightest sign of disintegration such as PAYEN observed, and after drying appeared practically unaltered. Assuming that the failure of this experiment might be due to the degree of vulcanisation of the sample being too high, another sample, vulcanised at 125° C. for two hours, was treated in exactly the same manner. This sample contained 1·9 per cent. of combined sulphur. The result, however, was exactly the same. In order to ascertain finally whether a desintegration of the kind described by this author could be effected by the action of his special solvent, the last named of the above mentioned samples, together with the solvent in which it had been immersed, was for a whole week heated to boiling point on a reflux condenser. This experiment also failed to produce the effect upon the india rubber described by PAYEN. The extracts obtained in every case consisted of the free sulphur contained in the sample, together with the resinous matter of the india rubber amounting to less than 3 per cent. of the mass of the sample operated upon.

A still more recent attempt to explain the vulcanisation phenomena is due to J. MINDER.[2] His fundamental views are expressed in the following three sentences :—

1. "Vulcanisation is produced by sulphur in the state of a vapour. In this form it penetrates into the rubber molecule, thus vulcanising the india rubber."

2. "Already at ordinary temperatures sulphur possesses a sensible vapour tension, which explains the fact that thin sheets of india rubber containing sulphur undergo spontaneous vulcanisation at ordinary temperature when left to themselves for a long time."

3. "In order to accelerate vulcanisation, the tension of the sulphur vapours, and their density, must be increased. This may be attained either by heating the sulphur and immersing the india rubber in it (sulphur bath) or by mixing the india rubber with sulphur and heating

the mixture (dry heat cure, steam cure), or by dissolving in a suitable solvent chemically combined sulphur vapours, and allowing such solutions to act upon india rubber."

These statements suffer from a certain vagueness of diction and want of definition. This particularly refers to the first of them, and so, by implication, to the second likewise, although they are, in my opinion unquestionably correct as far as they go. The third of these sentences I consider in every respect erroneous;* indeed, it is in part quite unintelligible. It is an everyday experience that to accelerate the vulcanisation process we must increase the temperature. This will incidentally result in an increase of the vapour tension of the sulphur, but we possess no evidence whatever that this vapour tension itself is the determining factor of the rate of vulcanisation. Vapour tension is a purely static condition which is devoid of any influence upon chemical reactions, although, if a change of vapour tension involves a change of the molecular*(chemical) state of the vapour, such an influence may become apparent, but is even then due entirely to the latter cause. So that, if we produce the latter change without changing the former, or even changing this in the opposite sense, the accelerating effect of the molecular change would nevertheless be there.

Entirely erroneous is MINDER'S view as to the necessity of increasing the density of the sulphur vapours in order to increase their vulcanising action, and still worse is his assumption that this increase of density can be achieved by raising the temperature of the sulphur vapours.

Equally unfortunate is MINDER'S explanation of the curing action of chloride of sulphur as quoted above in the third of his statements. To begin with, his description of chloride of sulphur as 'chemically combined sulphur vapours' is rather peculiar, and he altogether omits to explain why 'chemically combined sulphur vapours' should combine with india rubber at all. Indeed, the evidence of the scores of liquid and gaseous sulphur compounds, to all of which his description of the chloride of sulphur would apply likewise, would tend to prove that 'chemically combined sulphur vapours' do not combine with india rubber.

2. *Vulcanisation with Chloride of Sulphur.*—The process of vulcanising india rubber with chloride of sulphur—sulphur monochloride S_2Cl_2—was discovered by PARKES in 1846, and is now technically known as the 'cold cure,' to distinguish it from the 'dry heat cure' or 'steam cure,' as the processes of vulcanising with sulphur are variously called. It is carried out by treating the objects to be vulcanised with a from 1·5 to 3 per cent. solution of sulphur monochloride in carbon bisulphide. To a very limited extent, chiefly for the vulcanisation of certain kinds of double-faced sheets and waterproof cloth, a 'vapour cure' is also in use, in which the goods to be cured are hung in, or continuously carried through,

Krafft believes he has found in the chlorides of the aliphatic amines, for he finds[1] that hexadecylamine hydrochloride $C_{16}H_{33}.NH_2.HCl$ behaves in aqueous solution like a soap, in that the former boils without a temperature rise, whereas the solutions of the lower amines—*e.g.*, methylamine—show a considerable temperature rise, leading, like the salts of the low fatty acids, to values for their molecular weights of only half their theoretical amounts. Consequently Krafft comes to the conclusion that in aqueous solution the salts of the fatty acids, and those of the amines, are all, like soap solutions, more or less completely hydrolysed. This hydrolysis would, of course, double the number of molecules in solution, and thus account for the molecular weight being found too low by one half.

Krafft does not appear to admit that the phenomenon in question is perfectly satisfactorily accounted for by the theory of ionisation, nor does he recognise that his alternative explanation is hopelessly opposed to the fact that acetic acid can be titrated with caustic soda, as well as methylamine with hydrochloric acid. Moreover, if sodium acetate or methylamine hydrochloride are hydrolysed in their aqueous solutions, the former ought to possess saponifying, the latter inverting (to cane sugar), properties. Adopting Krafft's interpretation, we should have to assume also caustic soda to be 'hydrolysed' in aqueous solutions, which in the boiling test also yield values for the molecular weight of that base amounting to only one half of the real value—a fact entirely in agreement with the theory of ionisation, but utterly unintelligible in the light of Krafft's assumption. So much for Krafft's curious basis of his theory of the colloidal state.

Observing next that alcoholic solutions of sodium oleate exhibit a marked increase of their boiling point above that of alcohol—in other words, that the oleate in these solutions behaves as a crystalloid—Krafft infers that "water, at least under ordinary pressure, is as necessary for the formation of colloidal soap solutions as soap itself." With this statement one cannot but agree, but upon the real significance of this observation Krafft has nothing further to say. He then proceeds[2]:—

"The observation that such well-known organic salts, the composition of which is known beyond doubt, are capable of forming colloidal solutions, and therefore belong to the class of colloidal bodies, is of considerable interest in view of the fact that the nature of all colloid substances is still more or less wrapped in mystery. Particularly the observations made on hexadecylamine chlorhydrate $C_{16}H_{33}.NH_2.HCl$ and methylammonium palmitate $C_{16}H_{31}O_2(NH_3.CH_3)$ seem to confirm that although a not inconsiderable size of molecule seems to be essential for the formation of a colloidal substance, the chemical composition of the latter may nevertheless, be a very simple one."

In the first instance, I would point out that we have no right to call the soaps colloidal substances; they are very well defined crystalloids, which may or may not form colloidal solutions, according to the nature of the

[1] *Ber.*, xxix. (1896), p. 1331. [2] *Ibid.*, xxix. (1896), p. 1335.

solvent employed. If we call the crystallisable sodium salts of the fatty acids colloidal bodies, why not also aluminium chloride and ferric chloride, seeing that aluminium hydrate and ferric hydrate can also exist in colloidal 'modifications'? The very fact that an aqueous solution of sodium palmitate is a colloidal solution, but that an alcoholic solution of the same salt is a crystalloid solution, is proof conclusive that sodium palmitate itself is not a colloid, but a body which may undergo in aqueous solution a change leading to a colloidal solution. KRAFFT's expression of surprise that such simple salts as the ones he mentions are capable of forming colloidal solutions is peculiarly inappropriate, considering for how long a time colloidal alumina, ferric hydrate, and arsenious sulphide have been known, and considering further that we know quite a number of colloidal elements. It is, moreover, incorrect to say that to be able to assume the colloidal state, a substance must possess a high molecular weight. The very existence of all the inorganic colloids disproves this assumption. The colloidal molecule, no doubt, is always extremely complex, but it often, if not generally, consists of very small molecular units.

KRAFFT now advances the proposition: "Colloidal liquids or solutions contain the liquefied substances in the molecular state." The proof of this proposition he finds in the fact, as presented by him, that the salts of the low fatty acids in aqueous solution are hydrolytically dissociated, and consequently, in the determination of their molecular weights, yield figures amounting to only one half of their known molecular weights. The sodium salts of the high fatty acids are, in aqueous solution, likewise hydrolysed; but in spite of this, the boiling points of these solutions are identical with the boiling point of water, or, in other words, these salts exhibit the properties of colloidal substances. On the other hand, KRAFFT observed that the melting and solidification points of colloidal soap jellies are identical with the same constants of the respective fatty acids contained in these salts. He further observed that the molecules of the liquid fatty acids in question are exactly normal, and from these observations he concludes that the soap jellies also contain the free fatty acids, and so, by implication, also the soaps themselves, in the unimolecular state.

KRAFFT, of course, realises that his conclusions bring him into conflict with the laws and phenomena in relation to the osmotic pressure of solutions, and this difficulty he attempts to bridge over by a second proposition: "Molecules in the state of colloidal liquefaction rotate in small closed curves or surfaces." This curious conception would, of course, fairly account for the fact that colloidal molecules no longer appear to obey Avogadro's law, but this hypothesis calls just as much for explanation as do the facts it was invented to explain. The need for it simply arises out of KRAFFT's first proposition, with the truth of which it stands or falls. But the fact that the melting and solidification points of colloidal soap jellies are approximately identical with the melting and solidification points of their respective fatty acids, although a very interesting observation, scarcely

justifies KRAFFT's revolutionary conclusions. It is, indeed, by no means so certain that in these concentrated soap jellies the soaps are, as KRAFFT assumes, completely hydrolysed—at any rate, this assumption should not be made without further experimental evidence, which might have been obtained by the determination of the conductivities of these jellies. Nor should it be overlooked that it is even doubtful whether soaps, simple as is their composition, are really the best starting-point for a study of the colloidal state. For the same reason the salts of aluminium, iron, and chromium, from which colloidal hydrates are readily obtainable, or the silicates, or arsenious acid and its conversion into colloidal arsenious sulphide, would appear far more suitable objects. But there is, I conceive, one point which appears to me to call for careful consideration in enquiring into the causes and nature of the change of crystalloid into colloidal solutions—a point which, I think, should not be so summarily dismissed as has been done by KRAFFT. This is that in all these cases the colloidal state is induced by hydrolysis in aqueous solution. In this fact KRAFFT sees no more than what is expressed by the bare equation by which the chemical effect of hydrolysis is recorded :—

$$C_{16}H_{31}O_2Na + H_2O = C_{16}H_{32}O_2 + NaOH.$$

But the facts in connection with aqueous soap solutions, the conditions under which all the inorganic colloidal solutions and colloids are formed, the behaviour of the colloidal carbohydrates, and many similar considerations, all strongly suggest that the water plays a far more important and determining part than is expressed by a mere hydrolytic equation. Indeed, I am inclined to think that simple as the composition of the soaps and of the above named inorganic compounds appears, this is really a simplicity of a pragmatical order only, the simplicity of our ignorance; and that, in reality, the colloidal change induced in the above named substances by hydrolysis is an extremely complex phenomenon, and for this reason much more difficult to investigate than the nature and cause of the colloidal condition of a hydrocarbon substance like polyprene.

KRAFFT has shown[1] that by treating aqueous soap solutions with toluene, the whole of the fatty acid contained in the solution can be removed by successive extractions with that solvent. But from this it cannot be concluded that aqueous soap solutions contain the whole of the fatty acid in the free state. Indeed, according to his own showing,[2] this is not the case. An equilibrium, determined by the quantity of water present, and probably also by the temperature, is produced in these solutions :—

$$C_{16}H_{31}O_2Na + H_2O \rightleftarrows C_{16}H_{32}O_2 + NaOH.$$

But even at enormous dilutions this hydrolytic action is never complete, as is shown by a glance at the following curve (fig. 2) showing the per-

[1] *Ber.*, xxvii. (1894), p. 1752. [2] *Loc. cit.*, p. 1751.

centages of sodium contained in crystallisations obtained from solutions of various strengths of sodium palmitate.

These facts KRAFFT utilises for his theory, laying great stress upon the free acid and the free alkali in his colloidal soap solutions, but giving no further consideration to those portions of acid and alkali which remain in combination. He seems, on the strength of his observations of the result of the extraction of soap solutions with toluol, to assume that practically the whole of the soap in the solution is split up into free acid and alkali. But from his experiments it is perfectly obvious that this extraction simply disturbs the above mentioned equilibrium by the gradual abstraction of one of the constituents. He therefore entirely overlooks the highly significant fact that it is impossible to obtain his colloidal soap solution in its ideal state of purity by trying to prepare an aqueous and colloidal solution of pure palmitic acid.[1] He ignores that this is only possible if there be any alkali present, and from this fact I prefer to conclude that the colloidal state of a solution of sodium palmitate is induced in the first instance by the hydrolysis of that salt, which process,

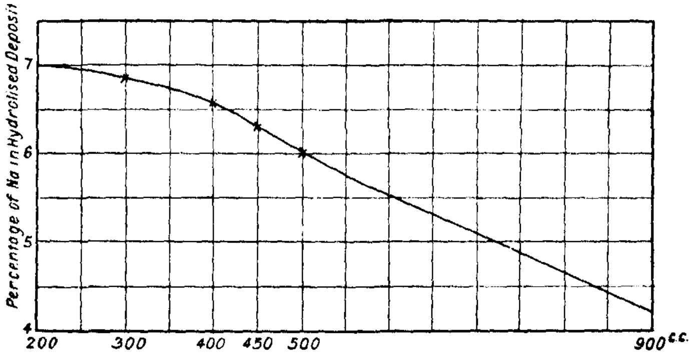


FIG. 2.—Diagram to KRAFFT'S theory of the colloidal state.

even at very great dilutions, does not appear to proceed appreciably beyond the formation, besides free alkali, of the dipalmitate $C_{16}H_{31}O_2Na + C_{16}H_{32}O_2$. With the formation of this latter salt the conditions for the colloidal state are obtained, but whether this salt is *eo ipso* a colloid, or forms a colloidal aggregation product with water, is not known, although I strongly incline to the latter conception.

Exactly the same is to be observed in the case of the salts of aluminium and iron, which in absolute alcoholic solution can be dialysed without the slightest decomposition. The dialysis of aqueous solutions of these salts, on the other hand, always yields the solutions containing what is known as colloidal alumina and colloidal ferric hydrate. To the well-known fact that these solutions always retain slight quantities of acid I have

[1] This may be attempted by dissolving palmitic acid in acetone, and diluting this solution with a large volume of water.

already drawn attention, and I strongly believe that the presence of this acid residuum should be looked upon, not as incidental, but as very probably playing a determining part in the subsistence of the colloidal state in the above named bases. Aluminium hydrate and ferric hydrate in the pure state no more form colloidal solutions than does pure palmitic acid: *the presence of a very small proportion of acid in the former, or of alkali in the latter, case appears to be essential. If this be correct, we arrive at the conclusion that neither the salts of aluminium, nor of iron, nor the pure hydrates of the oxides of these bases, nor the soaps, nor their free fatty acids, are colloids, but that they are all capable of forming colloidal aqueous solutions, the colloidal state being induced by the hydrolysis of these salts, and becoming the more pronounced, the nearer this hydrolysis approaches its chemical limits. Corresponding to the chemical lability of these salts is the peculiar physical instability of their aqueous solutions.*

How far these conclusions apply in regard to the silicates and colloidal silicic acid, to the tungstates and colloidal tungstic acid, and to colloidal arsenious sulphide, no observations are at hand which would enable us to form an opinion. It is, however, known[1] that on dialysing potassium silicate, gelatinous silicic acid is deposited on the septum, which fact suggests that alkaline silicates, like soaps, undergo hydrolysis in aqueous solution. On the other hand, colloidal solutions of silicic acid persist even in the presence of excess of acid; and silicic acid obtained by dialysis is, to the extent of 14 per cent., soluble in water[2]—facts which distinguish colloidal silicic acid rather sharply from the before discussed colloidal solutions. The facts in respect of tungstic acid are somewhat similar. Both the silicates and the tungstates are characterised by the enormous molecular complexity of their salts—polysilicates, polytungstates; and this fact must appear highly suggestive in view of the evidence we have been quoting in support of the assumption of high molecular complexity and distension of the colloids as a class. It is, indeed, remarkable that stannic acid, which possesses, though in a somewhat lesser degree, the above mentioned characteristics of silicic and tungstic acid, is also known to exist in a colloidal form. All three acids are rather weak acids, and in this relation it is important to observe that amongst the many colloids there is neither a strong acid nor a strong base. As a matter of fact, a considerable number of organic colloids, including some of the most typical members of this class, are either essentially polyalcoholic bodies, or simply hydrocarbons.

No doubt the unquestionable difference in the chemical conditions conducive to the induction in inorganic compounds of the colloidal state, as well as of its persistence when established, render it difficult to discover the determinant cause of the colloidal state; and this difficulty would seem to be increased by any attempt to explain the remarkable difference of the stability of the colloidal condition in the above named substances. The

[1] BECQUEREL, C. R., 67, 1081. [2] CHURCH, *Journ. Chem. Soc.*, 15, 107.

very facts in relation to these questions render it, however, obvious that the colloidal state is a purely physical condition induced in different substances by a number of rather varying chemical reactions. *The presence of water is the only condition common to all the cases of colloidal induction* we quoted or might have quoted, and in every one of these cases we are therefore justified in assuming hydrolysis or hydration as a contributing factor. Nevertheless, we are not justified in concluding from this that hydroxyl groups must be present in all colloids, for one of the most pronounced colloids, india rubber, is a hydrocarbon. Indeed, the induction of the colloidal state in the above discussed inorganic compounds, and probably in all ionisable compounds, *does not appear to be determined by any definite chemical composition, but rather seems to represent the physical corollary of a more or less limited phase in the decomposition of a reversible system.* With this conception of colloidal induction as the physical concomitant of an unstable chemical equilibrium, the fact that this induced colloidal state ceases to exist as soon as the chemical equilibrium to which it is due is disturbed by the intervention of some definite chemical influence, is in thorough agreement. Thus we know that as soon as we disturb the chemical equilibrium expressed by

$$C_{16}H_{31}O_2Na + H_2O \leftrightarrows C_{16}H_{32}O_2 + NaOH,$$

by abstracting gradually the palmitic acid by means of toluol, the colloidal state rapidly disappears in the realisation of the final condition of

$$C_{16}H_{31}O_2Na + H_2O = C_{16}H_{32}O_2 + NaOH.$$

In the great majority of other cases, the addition of small quantities of indifferent salts, or of acids or alkalies, disturbs the colloidal state by disturbing the equilibrium to which it is due, and at which only it persists. For this reason I hold that it is inadmissible to apply the term 'colloid' to substances which only within a more or less limited phase in a continuous series of physical changes induced by chemical differentiation can assume the colloidal state. Or, in other words, it is utterly misleading to describe as colloids compounds which in themselves are unquestionably crystalloids, and which exhibit colloidal characteristics only when forming part of certain chemical systems. Obviously in such cases the colloidal nature is due to the system as a whole, and not to any one of its components. *The term colloid should therefore only be applied to compounds, the solutions of which, under all conditions, and in whatever solvents, behave as colloidal solutions, and which further maintain this character through all chemical changes which leave the molecule, such as we conceive it, intact.*

Of course it might be argued that the globomorphous precipitates obtainable from the colloidal solutions of the soaps, of the salts of aluminium, iron, chromium, silicic acid, tungstic acid, stannic acid, and others, are the solid forms of the colloidal states of these compounds. This, however, would be tantamount to the assumption that the amorphous and the solid colloidal states represent essentially identical forms of matter—quite

an unacceptable proposition. The globomorphous form of precipitate is extremely common amongst the precipitates formed in a solution by a sudden and radical change of the composition of the solvent, but it has never yet been suggested that these globomorphous precipitates in any way represent a colloidal state of the substances precipitated. On the other hand, there is no doubt as to the close relationship between these globomorphous precipitates and the amorphous condition of matter in general; but in a vague way it is realised that there is a considerable difference between the amorphous state of matter in general and the equally amorphous solid colloids. Very little is known respecting this highly complex problem, but a careful study of the changes involved in the transformation of a colloidal solution into a jelly, and of such a jelly into a globomorphous or amorphous precipitate, will readily produce the conviction that the latter change involves an abrupt physical change such as is scarcely consistent with the assumption of the persistence of the colloidal in the globomorphous or amorphous state of matter. That there exists, nevertheless, a close connection between these very obscure states of matter is as certain as the fact that under certain conditions crystalloids, even in the crystalline form, as well as colloids, may assume globomorphous forms and structures.[1] All this, however, merely goes to show that the obscurity enshrouding the nature of colloidal solutions becomes utter darkness as we proceed from such solutions to globomorphous, amorphous, and colloidal solids. This fact is scarcely surprising, seeing that our knowledge of the nature of the gaseous state and of crystalloidal solutions is incomparably in advance of our insight into the constitution of solid crystalloidal matter.

But there are two states of colloidal solutions which are clearly recognisable as continuations of the colloidal state in solutions. These are the gelatinous and pectous states, both of which are familiar to everybody.

In the gelatinous state we have a colloidal solution assuming a peculiar state of semi-rigidity or quasi-solidity. The degree of rigidity of a jelly appears to be determined by the concentration of the gelatinising colloidal solution, and by the temperature. With the concentration, and with falling temperature, the rigidity increases; and it decreases, or even entirely disappears, with rising temperature. The change from the liquid colloidal to the gelatinous state is absolutely continuous, the solution losing gradually its fluidity until eventually the individual parts of the solution can no longer change their positions freely and independently, but become more or less rigidly fixed in relation to one another. It is well known that the peculiar physical properties of jellies can be explained by the assumption that every particle of the solution moves in extremely minute closed curves. Indeed, Lord Kelvin has experimentally demonstrated that by setting water into a state of 'fine grained vortex motion,' or 'vortex sponge,' it

[1] This has been abundantly demonstrated by Bütschli in his remarkable works *Ueber Strukturen* (Leipzig, 1898) and *Unters. über die Mikrostrukturen des erstarrten Schwefels* (Leipzig, 1900).

assumes all the properties characteristic of a jelly. It will at once be seen how closely this conception of the gelatinous state, a particular form only of the colloidal state, approximates to KRAFFT's theory of the nature of the colloidal state in general, and very likely this author drew his inspiration from this vortex theory of the ether. This application of this theory to the colloids as a whole suffers, in the first instance, from the difficulty that while this vortex theory might well be used to explain the phenomena exhibited by colloidal jellies, it would also seem to suggest that the gelatinous state is the only state in which colloids can and do exist. But this is not at all true—indeed, there is a number of undoubted colloids, india rubber being probably the best known of them, which have never been observed to assume the form of a jelly. A second, and at present perhaps even more formidable, difficulty lies in the fact that the application of the vortex atom theory to the explanation of the constitution of matter suffers from as yet insuperable mathematical difficulties.[1]

The property of cementation is one of the most characteristic properties of the colloids while they are in that peculiar metastatic condition which we discussed above as the gelatinous state. This property of cementation, or, in other words, the complete absence of, and the tendency to obliterate, possible cleavage planes, is also very probably one of the reasons why colloids have no solubility, and instead of dissolving in their so-called solvents in the manner of the crystalloids, gradually resorb them, swelling into jellies which eventually begin to flow, the resorption of the solvent still proceeding. This metastatic condition and property of cementation of the colloids is entirely absent in what GRAHAM termed their *pectous* modification. The passing of a colloid from either the state of a solid, or a jelly, or a solution into the pectous state at once terminates its metastatic condition, its capability of cementation. The wide range of sensibility of the colloids to physical and chemical influences becomes greatly restricted; or conversely, the physical and chemical indifference of the colloids is strikingly enhanced in the pectous state. A reversion from the pectous to the metastatic state of the colloid is therefore either impossible, or, when possible, does not reproduce the original colloid condition. Attempts to affect the pectous colloid by physical or chemical agents very frequently result in its physical and chemical break-down. A number of highly

[1] This is also, at any rate, largely the reason why the vortex atom has not already consigned the utterly unthinkable and unphilosophical atomic theory to the already well-stocked lumber-room of science. Incidentally it may be mentioned here that the conception of vortex atoms and of material masses as crowds of vortices is by no means of entirely modern date, but has had, like the theory of the hard material atom, several precursors. Particularly lucid and definite in this respect is MALEBRANCHE (*Recherche de la Vérité*, 1712):—"Preuve de la supposition que j'ai faite: Que la matière subtile ou éthérée est necessairement composée de petits turbillons, et qu'ils sont les causes naturelles de tous changements qui arrivent à la matière; ce que je confirme par l'explication des effets les plus généraux de la physique, tels que sont la dureté des corps, leur fluidité, leur pesanteur, leur légèreté, la lumière et la refraction et réflexion de ses rayons."

important technical processes, such as the tanning of leather, the vulcanisation of india rubber, the printing of pigment colours in albumen thickenings upon calico, are based upon these facts.

The pectous condition of a colloid or colloidal solutions may be induced—

(*a*) By heat. Colloidal solutions of alumina, ferric hydrate, chromic hydrate, and some of the albuminoid bodies are pectised by heat. The pectisation in this case is probably due to dehydration or intramolecular condensation. The presence of water, at least in the case of the albumens, appears to be essential, since it has been demonstrated that most carefully dried albumen is not pectised even at temperatures considerably above its coagulation temperature.

(*b*) By internal change (spontaneous action). Almost all the inorganic colloidal solutions, and also a few of the organic colloids, of the classes of the carbohydrates and albuminoids are able to pectise spontaneously. It is highly probable that pectisation in all these cases is due to a process of condensation and dehydration.

(*c*) By indifferent salts. That many colloids are precipitated from their solutions by the addition of generally very small quantities of so-called indifferent salts is well known, but whether these precipitates are generally, or even frequently, pectous is to me a matter of some doubt. GRAHAM certainly considered them as such.

(*d*) By chemical interaction between colloids. The solutions of acid colloids on the one hand, and of basic colloids on the other, mutually precipitate each other. The products thus formed are often very remarkable, and their systematic study offers a great field to scientific workers and technologists alike. Whether, however, these colloidal salts represent always pectous colloids is a question involving some uncertainty—an uncertainty largely due to a certain indefiniteness attaching to the definition of the pectous state. But in all those cases where pectous colloids are produced by either a process of substitution or of addition, we obtain products which very clearly exhibit all the above named characteristics of the pectous state.

The change of a colloidal solution to the gelatinous, from this to the pectous, and subsequently to the solid colloidal state, represents a continuous physical change without any abrupt break, although the appearance of the pectous state, as has already been pointed out above, is probably always due to a chemical change in the colloid. In this series of changes, as described above, the pectous state need not occur at all, its appearance being mostly determined by specific physical and chemical conditions, and in this case we pass gradually from the gelatinous direct to the solid colloidal state. It follows, therefore, that in the latter series of changes—liquid, gelatinous, solid—the order must be reversible; and that in the former

series—liquid, gelatinous, pectous, solid—this order cannot be reversed, owing to the non-reversibility of the pectous state. All these points are much more clearly exhibited by the organic than by the inorganic colloids. Indeed, the only substances which throughout a long series of chemical changes preserve their colloidal characteristics are the organic colloids. What in the inorganic colloids, including the salts of organic acids and organic bases, represents a mere transient phase, becomes in the organic colloids the permanent physical condition of their existence.

Thus far we find ourselves without any satisfactory working hypothesis as to the nature of the colloidal state, upon the basis of which the further exploration of this exceedingly interesting field might be pursued. We have so far only established the fact that the molecular weight of all colloids is extremely high, with the characteristic qualification that in the case of a great number of inorganic colloids it is a very high multiple of the normal molecular weight. This is the unavoidable conclusion to be derived from the behaviour of the colloids in the BECKMANN test, as well as from PFEFFER'S and LINEBARGER'S investigations on the osmotic pressure of colloidal solutions.

There are, however, some other points in connection with the physical behaviour of colloidal solutions which are capable of throwing some further light on their nature. The longest known of these is the fact that a great number of colloidal solutions, though by no means all, scatter polarised light in a direction at right angles to that of a pencil of light passing through them. This phenomenon, which was discovered by TYNDALL, was extensively studied in its application upon colloidal solutions by PICTON and LINDER.[1] The most convenient way of observing it I found to be by means of the arrangement shown below :—

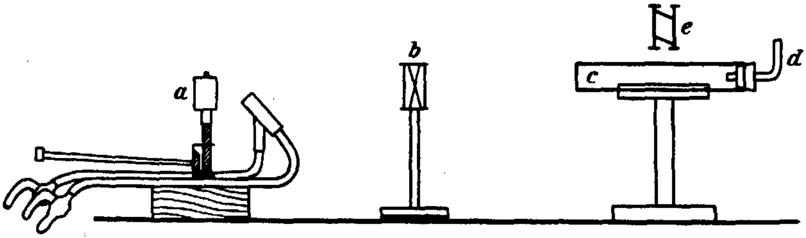


FIG. 3.—Disposition of apparatus for the observation of the 'Tyndall effect.'

a is a lime light jet, which is, of course, preferable employed enclosed in a lantern; *b* is a condenser provided with an iris diaphragm,[2] the best distance of which from the incandescent lime is easily determined by actual experiment. *c* is a glass tube of about ⅝ inch inner diameter, the two ends of which have been ground perfectly smooth. One end, the left hand one in the drawing, is closed by cementing upon it a micro cover glass of

[1] *Journ. Chem. Soc.*, 1892, p. 137.

[2] The type of condenser frequently employed for micro-photographic work answers very well.

suitable diameter. The other end can be closed with a stopper *d*, in the perforation of which a piece of glass tubing, bent at right angle, is fixed. This allows the tube to be filled with the solution to be examined without leaving in the tube any air bubbles to obstruct the path of the light. The apparatus is so arranged that the pencil of light coming from the oxy-hydrogen jet passes through the condenser *b*, and traverses axially the tube *e* containing the colloidal solution under examination. The radially reflected light is examined by means of a Nichol's prism, which is fixed in some suitable support.

By means of this arrangement the 'Tyndall effect' may readily be observed on a large number of inorganic colloids in solution, but it is important to state that it is not observable in all inorganic colloidal solutions, and in some only if they have been prepared in some special way. The case of silicic acid is particularly notable in this respect.

Most colloidal solutions of low concentration can be filtered, but here also we observe some very marked differences respecting the ease with which different solutions of equal concentration pass through the same kind of filter paper. Solutions of colloidal sulphur, inorganic sulphides, some forms of colloidal silicic acid, molybdic acid, and many others pass through the filter almost as readily as water, and leave no sensible residue on the filter. Other solutions filter more or less difficultly, and some few scarcely at all. Exactly similar differences exist between the very numerous organic colloids.

Filtration through porous cells is a much more severe test, and it appears that, even under pressure, only very few of the colloids are capable of passing through this material. There is, however, a limited number of inorganic, and a somewhat larger number of organic, colloids which are capable of hydrodiffusion, although the rate of diffusion in every case is very small.

Of extreme interest is the fact, first observed by PICTON,[1] that in a few colloidal solutions examination with the microscope reveals the presence of solid particles. The following quotation from PICTON's paper well describes the microscopic aspect of a colloidal solution of mercuric sulphide :—

"At first it is impossible to make out anything beyond a dimly granular appearance; but gradually one becomes aware of exceedingly minute particles in very rapid Brownian movement. The apparently homogeneous solution is really the scene of ceaseless oscillations of innumerable solid particles, crowded together so closely that very little free path is left. Indeed, this last fact is the probable explanation of their being seen at all. In a dilute solution the motion most likely becomes so rapid as to render the particles invisible."

It will readily be perceived that the very high molecular weight of the colloids as a class is well borne out by their comparative chemical and physical indifference, the low osmotic pressure of their solutions, and

[1] *Journ. Chem. Soc.*, 1892, p. 137.

consequently their low rate of diffusion and the almost immeasurably small depression of their freezing points and the equally small elevation of their boiling points.

It is, however, quite obvious that although all these constants are all very low as compared with the corresponding constants of the crystalloid bodies, this is, after all, a matter of degree only, and there would not be the slightest difficulty of compiling for every constant a scale, the terms of which, without any appreciable gap, gradually proceed from the most characteristic crystalloids to the most typical colloids. But this being so, it is evidently a most objectionable procedure to erect a purely artificial barrier between crystalloids and colloids by describing the solutions of the latter as pseudo-solutions, or, worse still, as suspensions.

No doubt this mistaken view is largely based upon the fact that a great many colloidal solutions contain particles large enough to scatter light, and even, in some cases, to become visible under the microscope—optical properties which appear to be incompatible with our previous conceptions and experience of molecules. But, granted a sufficiently high molecular weight, the low osmotic pressure of colloidal solutions becomes a necessary corollary, and with it all the rest of those physical properties which at first sight appear to differentiate so clearly colloids from crystalloids. There remains then only the difficulty of admitting the possibility of the existence of molecules large enough to scatter light and, indeed, to come within actual vision.

But quite recently Lobry de Bruyn[1] has shown the futility of even this argument. This author calls attention to the fact that the smallest particles capable of polarising light are from fifty to a hundred times smaller than the mean wave length of light. Putting the latter at $0{\cdot}5\mu$, the diameter of these particles could therefore not be less than from 5 to $10\mu\mu$.

We are, however, able to determine the molecular diameters of several colloids on the basis of their molecular weights as determined by purely chemical methods.

By the cryoscopic method the following molecular weights were obtained:—starch, 25,000; albumen, 13,000 to 14,000; gelatine, 5000; dextrine, 3000 to 4000; inuline, 2200. But these figures have always been looked upon as rather doubtful, owing to the considerable experimental error involved by the application of the cryoscopic method to the determination of the molecular weight of colloidal substances. It is therefore important to point out that Brown and Millar,[2] in their valuable paper on starch, dextrine, and the successive hydrolysis of these bodies, arrived at the result that the molecular weight of soluble starch prepared by Lintner's method is at least 32,500, and that of dextrine 6500. In the course of their investigations on iodine starch, Rodewald and Kattein[3] deduced for starch a molecular weight of 32,700. The remarkably close agreement between

[1] *Rec. des Trav. chim. des Pays Bas et de la Belg.*, 1900, xix., 236, 251.
[2] *Journ. Soc. Chem.*, 75, 331. [3] *Zeit. Phys. Chem.*, 33, 579.

the last named and BROWN and MILLAR's figure will at once be perceived, as also the fair approximation of both these figures to the one obtained cryoscopically.

According to VAN DER WAAL's calculations, the diameter of gas molecules is about from 0·1 to 0·3$\mu\mu$, and the diameter of the molecule of chlorine was stated by JAEGER[1] as 0·66$\mu\mu$. Now, taking as our basis the molecules of water vapour, oxygen, carbon dioxide, and chlorine, with the respective molecular weights of 18, 32, 44, and 71, it will be seen that the molecular weight of starch is, roughly speaking, a thousand times heavier than the mean of the above. Assuming now, as an approximation, that the specific volumes of these molecules are equal, it follows that the diameter of the starch molecule in solution is $\sqrt[3]{1000} = 10$ times larger than that of the above named molecules, and therefore about 5$\mu\mu$. But this value is practically identical with the value deduced for the diameter of the particles which, in colloidal solutions, are capable of scattering polarised light, so that by entirely different and absolutely independent methods, we arrive at values of exactly the same order of magnitude.

From this extremely interesting exposition it follows that colloidal solutions which scatter and polarise a pencil of light passing through them, or which even prove themselves microscopically discontinuous, cannot for this reason be set apart as 'pseudo-solutions' or 'molecular suspensions.' The introduction of these conceptions can only have the result of altogether obscuring the clear fact that there exists at present no recognisable line of demarcation between crystalloidal and colloidal solutions. The discontinuity between these two so-called classes of solutions is only apparent, and a discontinuity of methods of perception rather than of phenomena.

LOBRY DE BRUYN[2] quite clearly realises this, but his proposal, based upon PICTON and LINDER's observation that colloidal solutions are non-electrolytes, to distinguish electrolyte and non-electrolyte solutions will, no doubt, in time share exactly the fate of the older distinction. It is certainly very striking that all the colloidal solutions, organic or inorganic, even solutions of colloidal silver, are non-electrolytes; but everything is in favour of the assumption that as we proceed from the high molecular colloidal solutions to the crystalloidal solutions, the phenomenon of ionisation, conductivity, will gradually appear and increase.

But if all this requires any further proof, there is the case of oxyhæmoglobin as given by PICTON and LINDER themselves. PREYER assigns to hæmoglobin the empirical formula $C_{600}H_{960}N_{154}FeS_3O_{189}$, which agrees very satisfactorily with MARSHALL's result, who, from the amount of carbonic oxide absorbed by hæmoglobin, determined its molecular weight as 14,157. Oxyhæmoglobin is a finely crystallisable compound, the scarlet solution of which in water (0·3 per cent.) very markedly exhibited TYNDALL's phenomenon. Nor was it possible to filter this solution through a porous cell: the filtrate obtained was absolutely colourless. We have therefore here a

[1] *Zeit. Phys. Chem.*, 82, 17.

[2] *Rec. des Trav. chim.*, xix., 255.

crystalline compound of enormous molecular weight exhibiting all the characteristics of the colloids.

Of course there is this difficulty, that probably all the inorganic, and perhaps also some of the organic, colloids represent high molecular aggregates of crystalloid molecules; and as the same is undoubtedly true of matter in suspension, this might appear a strong justification for the 'suspension hypothesis' of the colloidal state. But it is by no means certain that the high molecular organic colloids are merely aggregates of the crystalloid molecules as we conceive them. It is by no means certain that colloidal arsenious sulphide is simply $(As_2S_3)_m$, or colloidal silicic acid $(SiO_2)_m$. Indeed, as regards the latter, we have certain indications that this is not the case. GRAHAM's colloidal silicic acid showed only a faintly acid reaction, and 100 grms. of SiO_2 contained in it required for complete neutralisation only 1·85 grms. of KOH instead of 93·33 grms. Thus it would appear that in the colloid only one molecule of SiO_2 in fifty is capable of acting chemically as SiO_2. This appears to me a point of great importance, the further study of which is likely to throw considerable light upon the great chemical indifference of colloids.

There is, however, a further point which seems to afford strong proof of the very wide difference between a suspension and a colloidal solution. This is the remarkable fact that a very considerable number of crystalloidal precipitates formed by double decomposition of various salts cease to be produced when the precipitation is attempted in highly concentrated colloidal solutions, although double decomposition certainly still takes place. Some of the most insoluble precipitates are in this manner obtained, as was recently shown in an admirable paper by LOBRY DE BRUYN,[1] in an apparent state of perfect solution. It is utterly inconceivable that mere suspensions of high molecular aggregates could produce such a result.

Nor is the property of the colloids of gelatinising, or pectising, at all intelligible as a function of suspended matter. It is, indeed, when we enter upon the consideration of these two phenomena of the colloidal state that the difficulty of the colloidal problem becomes altogether overwhelming in the present condition of our knowledge.

The gelatinising of a colloidal solution must be clearly distinguished from the change GRAHAM termed pectisation. The gelatinous state of a colloidal solution, relative to the liquid state of solution, is characterised by its reversibility. The physical state of a colloidal jelly is essentially a function of concentration and temperature. A solution may be induced to gelatinise either by increasing its concentration or by lowering its temperature; and conversely, a jelly may be liquefied either by reducing the concentration or raising the temperature. For every colloid capable of gelatinising[2] there

[1] *Rec. des Trav. chim. des Pays Bas*, xix. (1900), 236.

[2] Only comparatively few of the known colloids are capable of forming jellies in the above sense.

seems, however, to exist a critical concentration, below which no reduction of temperature will induce gelatinisation.

From these facts it may safely be inferred that gelatinisation is an aggregation phenomenon resulting in the cessation of the free mobility of the colloidal molecules, and the fixation of their relative positions. Colloidal matter in the gelatinous state represents therefore a molecular sponge, and it becomes evident that colloidal matter in this state already possesses a definite structure, determined, no doubt, largely by the stereometric condition of the individual molecules, and, as I believe, in a minor degree also by the nature of the solvent.

This highly probable assumption explains also most satisfactorily the extraordinary microscopic reticular structures, of which we owe such admirable accounts to Prof. BÜTSCHLI. The conception of BÜTSCHLI'S colloidal structures—'Schaumstrukturen'—which are of an order of magnitude respecting their elements in most cases approaching the limits of microscopic vision, as molecular sponges likewise cannot be objected to on the ground of their visibility, since we already have to face the fact of actual molecules in solution coming within the limits of optical perception.

The pectous state of colloids is in its outward appearance often indistinguishable from the gelatinous state, but the two are sharply distinguished from each other by the circumstance that the pectisation of colloidal solutions is not a reversible process. Colloidal solutions can be pectised at very much lower concentrations than those required for gelatinisation, and in those cases where temperature is of any marked influence upon pectisation, this influence shows itself as the effect of a rise of temperature.

The influences which induce the pectisation of colloidal solutions are somewhat varied and certainly not easy to classify. Some colloidal solutions pectise spontaneously on standing, some by boiling, a large number of the inorganic colloids by freezing. The majority of the inorganic colloids pectise on adding to their solutions minute quantities of electrolytes, but in a number of cases the precipitates obtained are re-soluble in pure water, and therefore certainly not pectous.

The most typical cases of pectisation are those in which the colloid in solution forms a pectous jelly on undergoing a chemical change. Cases of this kind are extremely rare amongst inorganic colloids, but rather frequent among the organic colloids. The question of the change involved in the pectisation of a colloid is, on the whole, still a very obscure point, and the probability is, that it will ultimately be found to resolve itself into a group of partly physical, but mostly chemical changes.

As regards the physical condition of matter in a pectous jelly, it must obviously be described in exactly similar terms to those in which we have above described the constitution of a 'reversible' jelly. But the 'fixation of the relative positions' of the colloidal molecules in the case of the pectous jelly being due to a chemical change produced in the molecule, it would

only be reversed by reversing the chemical reaction in question, and not by a mere change of physical conditions, such as temperature or solvent.

Such a chemical change may, of course, be induced by purely physical agents, as in the case of albumen by the application of higher temperatures, in which case pectisation would be due to a process of condensation or dehydration; but in the majority of cases it is the result of a chemical reaction between the colloid in solution and an added chemical reagent.

While comparatively few only of the numerous organic and inorganic colloids are capable of forming reversible jellies, all are capable of forming pectous jellies. Indeed, even the solid colloids are pectised, rendered permanently insoluble, whenever we are able to induce in or throughout them a chemical reaction under the influence of some outside reagent. And this brings us into contact with a matter of extreme technical importance in regard to colloids—namely, the fact that the ultimate physical condition of every colloid in the pectous state depends to a very considerable extent upon the physical state of the colloid at the time pectisation was produced. *In other words, pectisation is the means of perpetuating any physical state of a colloid.* The vast majority of the most important technical problems in relation to colloids become intelligible once this fact is clearly realised.

There is one curious point to be noticed in regard of the pectisation of colloidal solutions. It consists in the fact that while colloidal solutions can be pectised—*i.e.*, converted into insoluble colloids—however great their dilution, pectous jellies can be obtained only with solutions the concentration of which does not fall below a certain limit, which differs not inconsiderably for different colloids.

It may at once be stated that these limits are, for the various colloids, very much beyond the limits of concentration determining the formation of reversible jellies in the different colloids; or, in other words, a colloidal solution will form a pectous jelly at a dilution at which the solution would no longer form a reversible jelly. But the concentration at which a colloidal solution has been converted into a pectous jelly leaves, nevertheless, its mark upon the colloid, so as to render it permanently distinguishable from any pectous jelly of the same colloid, but produced at a different concentration. Nor does this difference disappear if such different pectous jellies are, by desiccation or otherwise, freed from the solvents distending them. In fact, in most cases there remains a difference in their general appearance, their softness, often even their colour; and on re-immersing these different products in their former solvents, which cause them to swell or distend, it will be found that the volumes to which they are distended bear an evident close relation to the volumes they occupied before their pectisation.

Colloidal solutions subjected to a pectising treatment at concentrations beyond the limits above referred to, as already stated, no longer form pectous jellies, but simply amorphous precipitates, and it is

highly significant and suggestive that at whatever concentrations these precipitates have been produced, they behave physically and chemically exactly alike. One cannot help thinking that in colloidal solutions the individual molecules do not possess free mobility, but that the latter is impeded by a general action—attraction?—of all the molecules upon each other. This would necessarily lead to the displacement of any one molecule, or group of molecules, by an external force resulting in a corresponding displacement, but one decreasing with the distance from the centre of disturbance, of all the surrounding molecules. Such a conception appears to afford a satisfactory explanation of the often very striking viscosity of colloidal solutions, which often exhibits itself in such a peculiar form as to suggest that in colloidal solutions we are confronted with matter in a state of continuous molecular concatenation or aggregation. It likewise seems to me to explain the cause of the often enormous internal friction of colloidal solutions, and would suggest it to consist really in a molecular shearing stress. This peculiar molecular effect, which also exists in many highly concentrated crystalloidal solutions, would, of course, tend to decrease with the concentration, and would entirely disappear beyond a certain limit of dilution. The existence or disappearance of this state of molecular interaction would determine the capability, or the reverse, of colloidal solutions to form pectous jellies.

A hypothesis of this kind may or may not prove of service, but it suggests several highly interesting lines of experimental research which in any case would be productive of valuable results. The problem in question is, however, considerably complicated by the fact that the nature of the solvent itself by no means plays a passive part in the formation of a colloidal solution.

This is well exemplified in the case of india rubber, the viscosity of the solutions of which varies markedly with the nature of the solvent employed. And these differences seem to endure even after the separation of the solvent from the colloid. At any rate, india rubber separated. either by precipitation or by evaporation, from its solution exhibits considerable differences in its physical properties—notably in tensile strength—according to the nature of the solvent in which it was dissolved; and this fact I believe to be closely related to the further observation that a similar striking difference exists between the relative volume to which india rubber will swell in different solvents. These facts are matters of considerable technical importance.

Thus far the condition of matter in the colloidal state would appear to be simply that of matter possessing extremely large molecular weights, but not differing from crystalloidal substances by any *specific* physical or chemical characteristics. The transition from the crystalloidal to the colloidal state would, accordingly, appear to be perfectly gradual and continuous; and although the extreme terms of the series exhibit enormous physical and chemical differences, these become quite insignificant between

neighbouring terms. There is much in the facts known at present in reference to colloids to commend this view, but there are also certain properties of colloidal solutions, most of which have already been referred to above, which do not become more intelligible on this assumption.

Perhaps the most striking of these is the observation that colloids in solution, or in the state of a jelly, are capable of altogether preventing the formation of a great number of crystalloidal precipitates. This fact has long been known, but it was first studied more thoroughly by LOBRY DE BRUYN,[1] who showed that insoluble precipitates of a number of salts, which form by double decomposition, are no longer obtained if these solutions contain from 5 to 10 per cent. of gelatine. Double decomposition, indeed, does take place under those circumstances, but the products remain in colloidal solution. On cooling such mixtures, absolutely glass-clear jellies are obtained. LOBRY DE BRUYN obtained in this manner perfectly transparent colloidal solutions of metals (by reduction), sulphides, hydroxides, ferrocyanides, cuprous oxide, and manganese peroxide.

These facts are quite inexplicable on the above assumption. They show that colloidal solutions are capable of inducing the colloidal condition in normally crystalloidal precipitates at the moment of their formation. This very curious phenomenon is, of course, not incompatible with our above assumption, nor is it very likely that it conflicts with a property of colloidal matter which is not also shared by matter of a lower molecular weight, and which, indeed, may be a function of that constant; but even so, its explanation cannot be hoped for until our knowledge of the physics of matter of extremely high molecular weight has considerably advanced beyond its present state.[2]

[1] *Rec. des Trav. chim.*, 1900, p. 236.

[2] The further question as to whether the colloidal state is confined to the solid and liquid states of matter, or whether there is such a thing as a colloidal gas, I did not venture upon in the foregoing pages for very obvious reasons. At first sight this suggestion appears to be verging on the absurd, as it might seem to imply that colloids could be converted into gases. Of this no instance is known. But, on the other hand, TOWNSEND (*Proc. Camb. Phil. Soc.*, 1897) made the very curious observation that electrified hydrogen diffuses with extreme slowness through a porous pot—as Prof. J. J. THOMSON (*Discharge of Electricity through Gases*, p. 16, London, 1898) puts it, just as if an electrified particle were "the centre of an aggregate of some kind which is very large compared with the dimensions of a molecule." But this, according to the result we arrived at above, is exactly what would constitute a colloidal gaseous molecule. TOWNSEND filled dust-free electrified hydrogen into a porous pot: "The rate at which hydrogen in its normal condition escaped from the pot was determined, and then, by connecting the porous pot with an inductor connected with an electrometer, the rate at which the charge escaped from the pot was determined. If the electrical particles had been simple molecules, the rate at which the charge escaped would have been equal to the rate of escape of the hydrogen; whereas the experiment showed that in reality the rate at which the charge escaped was only a small fraction of the rate at which the hydrogen escaped." In other words, here we have hydrogen assuming properties which distinguish it from its normal condition, just in the same manner in which a crystalloidal substance is distinguished from its colloidal form. Whether TOWNSEND was operating with colloidal hydrogen in this case is a question of extreme interest. If so, we should

It is quite possible that experiments on the phenomena just discussed applied to india rubber would be capable of yielding highly interesting technical results, and would well repay careful study.

Outlines of a Theory of Vulcanisation.

India rubber, within a comparatively very limited range, displays great sensitiveness to changes of temperature. In the early stages of the manufacture of rubber goods this drawback was very keenly felt, and so was the further difficulty that india rubber surfaces have a great tendency to cling and unite, and that the plasticity of the material was very apt to lead to deformations. The 'tackiness' of india rubber, it was soon found, could be largely remedied by treating the surfaces with mineral powders, such as French chalk (talcum), precipitated calcium carbonate, or sulphur. But this would, of course, still leave the other difficulties to be felt. It is therefore not surprising that the early practical workers tried to devise a process to convert the crude india rubber into a, physically, more stable product. This was accomplished by treating india rubber with sulphur at temperatures exceeding 120° C., a process jointly credited to GOODYEAR in America, and HANCOCK in England. The process is now known by the not very felicitous description of *vulcanisation*.

The recent efforts of chemists to bring to bear upon the numerous operations and problems of the india rubber industry the methods and results of modern chemistry have repeatedly been made the subject of adverse criticism. The smallness of the results so far achieved has been contrasted with the enormous importance of the above named discovery of GOODYEAR and HANCOCK. Such criticism entirely overlooks the fact that this discovery was the result of years of experimenting, and was then, in the end, in the case of both discoverers, due far more to perseverance and accident that to rational method and insight. Of inventions and discoveries made in this more or less haphazard manner we only hear of the successes, but not of the countless failures. On taking possession of the india rubber field, the chemist found himself confronted by an enormous number of empirical, disconnected observations resting upon no other basis than that of daily rule-of-thumb routine. As regards the india rubber itself, quite apart from the phenomena encountered in its manufacture, nothing at all of any reliable, or even tangible, nature was known. In other words, the very basis had to be created for the scientific method to be applied. It is not usual that pioneer work of this kind leads to immediate revolutionary discoveries.

Often these same critics assure us that vulcanisation being a long accomplished fact, there is, indeed, nothing left for the chemist to discover concerning india rubber. This statement is made, be it noted, at a time

expect the vapour density of this electrified hydrogen to be very much higher than the vapour density of this gas in its normal condition. An experimental decision of this highly important point should not be very difficult.

when not one manufacturer out of ten has the faintest idea of the intrinsic nature of the process upon which he depends for his whole production, and when the same critical authorities cannot agree between them whether sulphur does or does not chemically combine with the india rubber in the vulcanising process, and even seriously state that india rubber contains liquid hydrocarbons, or that such are formed in the process of roller mastication.

We turn our attention first to the question of the general action of sulphur upon india rubber at higher temperatures, and it will be advisable to complete this enquiry by ascertaining at the same time the nature of the action of PARKES' cold vulcanising agent, sulphur monochloride.

The sulphur bath method might appear from several points of view the most suitable method of studying this question, but after a number of attempts, I abandoned it in favour of the method of subjecting carefully prepared homogeneous mixtures of Pará rubber with a definite amount of sulphur to the action of heat. Again in this case we have the choice of several methods of heating, but the one of heating pieces of this Pará mixture of uniform thickness to vulcanising temperatures when immersed in water appeared to me the most satisfactory, as it involves the minimum of loss of sulphur by evaporation.

The experiments were carried out with strips cut from a calendered sheet, 3 mm. in thickness, of a mixing of 100 parts of Pará rubber with 10 parts of pure precipitated sulphur. These strips were vulcanised in a phosphor bronze digestor of the construction shown in fig. 4.

The digestor is provided with a thermometer tube (thermometer in mercury), a pressure gauge, and a blow-off valve. In the digestor a porcelain beaker is suspended, so that it is clear of the bottom. The digestor is filled to about one quarter of its capacity with water; the beaker is completely charged with water, and a number of the strips to be experimented upon immersed in it. The digestor is then closed, rapidly heated to the required temperature, and maintained thereat, either by carefully adjusting the gas burner, or by means of some form of thermo-regulator. At regular intervals one of the strips is withdrawn after blowing off steam and rapidly opening the digestor, which is then immediately closed again to continue the series. The time error caused by these successive withdrawals does not exceed four minutes per sample. Of course the water lost by the blown-off steam is from time to time made up with boiling water.

The strips thus withdrawn are marked, and subsequently cut into very fine threads, which are freed from every trace of uncombined sulphur by extraction with acetone in a Soxhlet extractor. The greatest care was employed to render this operation perfect, every sample being subjected to a three days' continuous extraction. The extracted samples were dried in a current of carbonic acid in the water oven and, until analysis, preserved in carefully stoppered glass tubes.

About 1 grm. of each of these samples was used for analysis. The sulphur determinations were all, without exception, carried out by CARIUS' method, as the results by the much simpler and more expeditious method

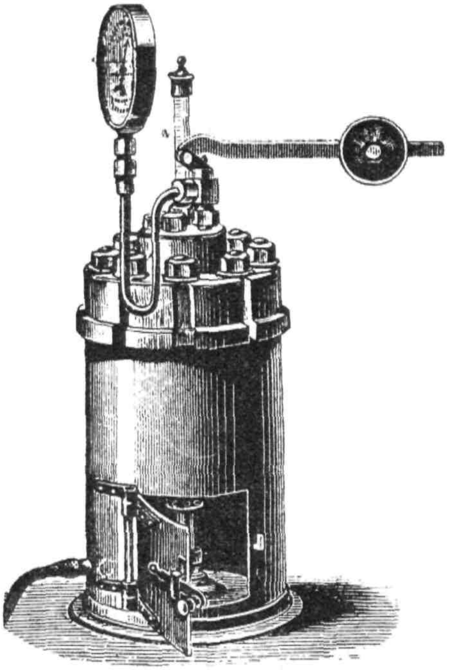


FIG. 4.—Digestor for vulcanisation experiments.

proposed by HENRIQUES (*see* page 253) were found to be liable to an error approaching − 0·1 per cent. in magnitude. In this manner the following results were obtained:—

VULCANISATION OF PARÁ RUBBER.

Duration of Vulcanisation.	Temperatures of Vulcanisation.				
	120° C.	125° C.	130° C.	135° C.	140° C.
	S. %	S. %	S. %	S. %	S. %
30 mins.	0·71	0·71	0·99	1·76	...
60 ,,	1·18	1·32	1·44	2·17	...
90 ,,	1·31	1·67	2·04	2·36	...
120 ,,	1·62	1·91	2·32	3·92	5·07
150 ,,	...	...	...	4·02	...
180 ,,	1·78	2·11	2·94	4·18	6·05
240 ,,	1·93	2·22	5·00	5·50	...
300 ,,	2·25	2·35	5·27	6·74	...
360 ,,	2·60	3·80	5·82	6·88	...
420 ,,	3·71	4·04	6·04	6·97	...
480 ,,	3·94	4·31	6·33	7·13	...

These figures amply suffice to demonstrate indisputably the fact, even quite recently again denied, that the vulcanisation of india rubber with sulphur involves the chemical combination of these two substances, at any rate as far as the vulcanisation of Pará rubber is concerned.

That different brands of india rubber behave very differently in the vulcanisation process is a well-known fact, but what we know at this moment respecting the composition and chemical relationship of these different brands entitles us to assume that, although their behaviour under vulcanisation may not be identical with that of Pará rubber, it will be more or less closely analogous to it.

Experiment entirely confirms this expectation, as is shown by the following tables, which show the effect of the vulcanisation of Lagos, Beni River, Ceara, and Borneo rubber at the temperatures of 125° C. and 135° C. respectively:—

VULCANISATION OF UPPER CONGO, BENI RIVER, CEARA, AND BORNEO RUBBER.

Duration of Vulcanisation.	Upper Congo.		Beni River.		Ceara.		Borneo.	
	125° C.	135° C.	125° C.	135° C.	125° C.	135° C.	125° C.	135° C.
	S. %	S. %	S. %	S. %	S. %	S. %	S. %	S. %
30 mins.	0·82	1·93	0·41	1·07	0·92	1·37	0·52	0·48
60 ,,	1·25	2·21	0·78	1·84	1·38	2·01	0·98	1·15
90 ,,	1·36	2·72	1·10	3·26	2·01	2·59	1·21	1·76
120 ,,	1·54	3·02	1·58	3·75	2·26	3·23	1·34	2·02
180 ,,	1·70	3·86	2·18	4·68	2·52	3·83	1·84	2·41
240 ,,	2·06	4·53	3·08	5·67	3·22	4 19	2·06	2·62
300 ,,	2·48	5·26	4·57	6·72	3·43	4·55	2·30	3·23
360 ,,	2·94	6·17	5·11	7·38	3·59	4·73	2·67	3·79
420 ,,	3·39	7·12	5·31	7·92	4·01	4·99	3·19	4·00
480 ,,	3·81	7·53	6·35	8·28	4·31	5·27	3·59	4·21

The extremely interesting results[1] here tabulated remove all doubt

[1] It is perhaps scarcely necessary to point out the interest and technical value of the above series and their graphic representations. They offer a means of reducing to a rational basis the factory practice in regard to the treatment in the vulcanisation of 'mixings' containing different brands of india rubber. They show by simple calculations which brands may, with advantage, be combined in a 'mixing' to produce an article possessing any desired physical properties, and they show conversely also which brands will not produce a satisfactory blend.

In this matter the manufacturer has so far been guided by practical experience alone, which may have been satisfactory in a number of cases, but leaves it an open question whether the best possible result has really been obtained. In other cases, there is no doubt, the blending of different brands of india rubber is made a matter of price merely, which, as the above tables clearly show, is unquestionably the worst procedure imaginable, and one that must often lead to sheer waste of individually good material.

Of course before these tables become generally useful it will be necessary to work out the same series for all important brands of india rubber, and, with advantage, for a larger range of temperatures; and it will further be necessary to determine for each series from point to point the mechanical strength of the test pieces.

that the vulcanisation of india rubber is a chemical process resulting in the formation of a polyprene sulphide. The rate at which the sulphur enters into combination with the india rubber hydrocarbon (polyprene) is characteristic for each brand of india rubber. Some of the above series were repeatedly investigated, always with the same result. The different behaviour of the various brands is particularly striking in the graphic representations, figs. 5, 6, and 7.

There arises now, of course, at once the question as to the nature of

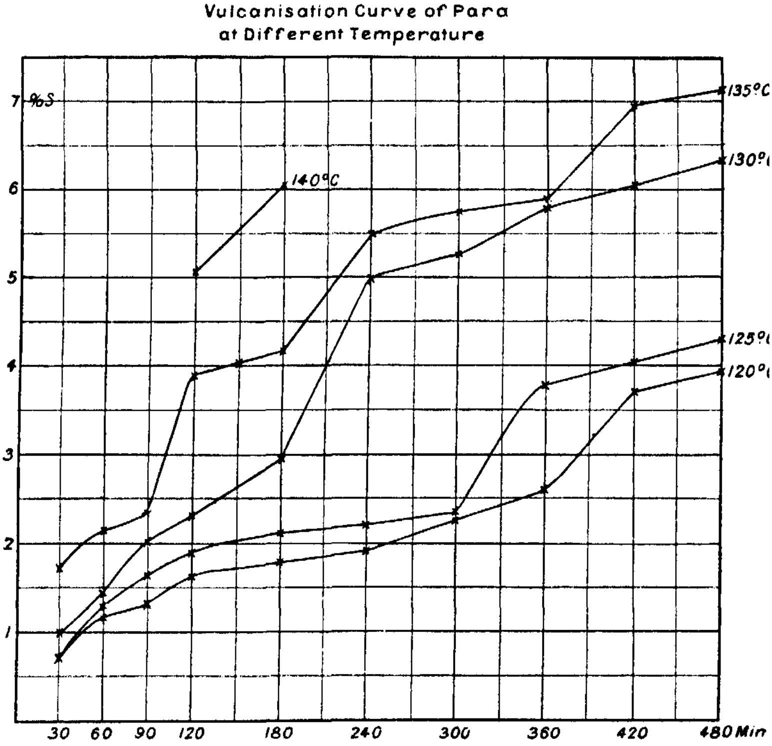


FIG. 5.—Vulcanisation curves of Pará.

the process by which sulphur enters into combination with the polyprene, whether the polyprene sulphide or sulphides formed are addition or substitution products. Certainly what we already know respecting the chemical nature of india rubber leads us to infer that the vulcanisation process consists essentially in the formation of an addition product of sulphur and polyprene. This assumption, however, requires further support in view of the fact that quite a number of writers, from PAYEN to most of the recent authors, declare that vulcanisation is accompanied by evolution of sulphuretted hydrogen, thereby implying that the process is a substitution, and not an addition, process. Indeed, most of the recent

authors on this subject state this in so many words. We shall therefore have to subject this point to a careful examination.

Assuming the compound of polyprene and sulphur, which indisputably forms in the vulcanisation process, to be a substitution product, it follows with absolute necessity that for each 32 parts of sulphur combining with the polyprene, we must obtain 34 parts of hydrogen sulphide. Now, in the process of vulcanisation as practically carried out, we obtain, on an average, a product containing, say, 2·5 per cent. of combined sulphur. Consequently the vulcanisation of one ton of india rubber, on the above assumption, would

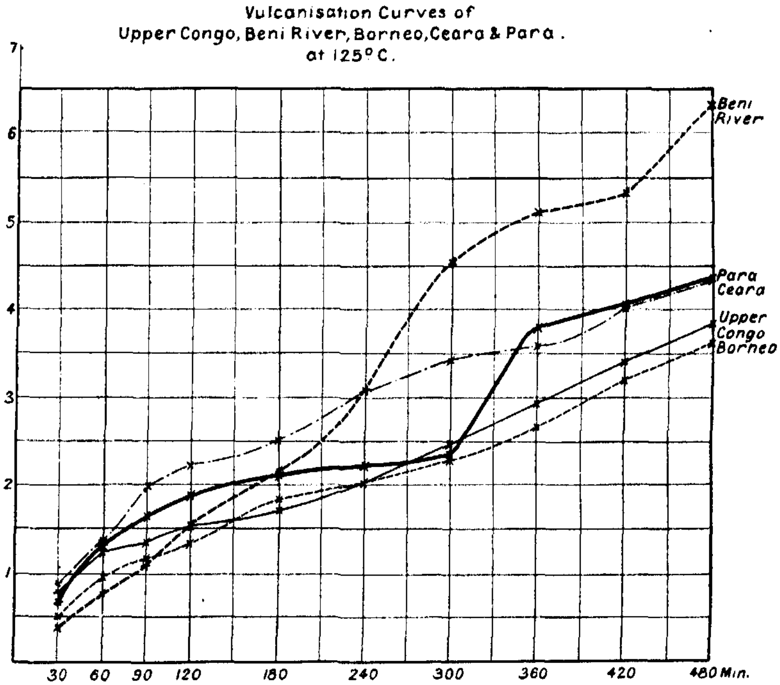


FIG. 6.—Vulcanisation curves of Pará, Congo, Beni River, Ceara, Borneo, at 125° C.

be bound to yield very nearly 60 pounds of hydrogen sulphide, or approximately 18,000 litres. Considering that in a number of factories the amount of india rubber vulcanised daily largely exceeds one ton weight, we should expect to find the vulcanising rooms of these factories reeking with this gas. As a matter of fact, however, there is scarcely ever a trace of this gas to be discovered in the rubber works' atmosphere, and the very rare cases in which its presence becomes noticeable may always be considered as an indication of something 'having gone wrong.'

In the vulcanisation of 'hard rubber' goods (ebonite, vulcanite) faint but distinct traces of sulphuretted hydrogen are generally, perhaps always, observable, but they could not be ascribed to the vulcanisation process proper—

the combination of polyprene with sulphur—which process, if it consisted in the substitution of hydrogen by sulphur, should cause a perfectly torrential evolution of hydrogen sulphide, seeing that 'hard rubber' contains at least 20 per cent. of combined sulphur.

It is therefore certain that if hydrogen sulphide forms at all in the vulcanising process, its amount is utterly inadequate to support the assumption that the process of vulcanisation is a substitution process.

Laboratory experiments on this question lead to exactly the same

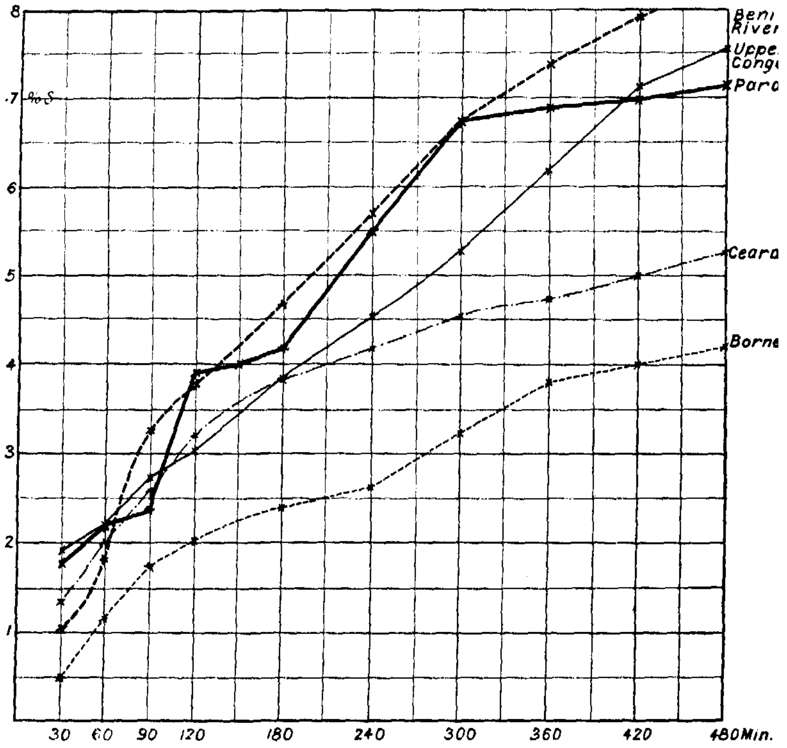


FIG. 7.—Vulcanisation curves of Pará, Congo, Beni River, Ceara, Borneo, at 135° C.

conclusion. If the experiments are carried out with technically pure Pará rubber under conditions absolutely precluding the escape of any gaseous product of the reaction, very minute traces of hydrogen sulphide may sometimes be observed; but in a considerable number of carefully devised experiments with highly purified Pará rubber, no hydrogen sulphide at all could be detected.

If, on the other hand, the 'insoluble' part of india rubber is mixed with sulphur, and this mixture subjected to vulcanising temperatures—say, about 135° C.—a considerable evolution of hydrogen sulphide takes place due to the formation of a substitution product of this insoluble body, $C_{80}H_{68}O_{10}$,

with sulphur. This substitution process certainly proceeds much slower than the vulcanisation process of india rubber (polyprene). Under the same conditions of temperature and time under which polyprene forms a vulcanisation product containing 4 per cent. of sulphur, the above named insoluble constituent forms a substitution product containing at most 0·7 per cent. of sulphur.

From these facts we are entitled to draw the following conclusions :—

1. *The india rubber hydrocarbon, polyprene* $C_{10}H_{16}$, *combines with sulphur without evolution of hydrogen sulphide. The vulcanisation process of india rubber is therefore an addition process.*

2. *The insoluble constituent of india rubber, which forms only an insignificant proportion of the technical product not exceeding 5 per cent. of the total, combines with sulphur under vulcanising conditions at a very slow rate with evolution of hydrogen sulphide, and with the formation of a substitution product.*

The above conclusively settles the question regarding the general chemical aspect of the vulcanisation process, but it confronts us with the further question respecting the quantity of sulphur combining with india rubber in this process, as well as the more intimate structure of the compound thus formed.

The tables on pages 84 and 85 very distinctly show that the reaction taking place between polyprene and sulphur leads to polyprene sulphides with an increasingly larger proportion of sulphur, without at any time any very distinct break in the rate of progression of the reaction being noticeable, which break might be interpreted as an indication of the formation of a definite compound. Indeed, one might be tempted to explain the very curious irregularities in the vulcanisation curves of Pará rubber, as given on page 84, in the above suggested sense, but on closer examination it will be found that by carrying out the vulcanisation at different temperatures, these irregularities appear at very different places, and therefore may be taken as probably indicating a particular physical, rather than some definite chemical, condition of the vulcanisation product. In this relation attention may be drawn to the tabulated results and curve plottings in reference to the vulcanisation of Beni River, in which case no sudden rise of the vulcanisation coefficient, and consequently also no irregularities in the corresponding curves, are to be observed.

In the presence of a very large excess of sulphur, and at temperatures between 135 to 150° C., vulcanisation proceeds at a still more rapid rate, and the amount of sulphur combining with the polyprene increases enormously, leading to the formation of products technically known as 'hard rubber,' ebonite, or vulcanite. The formation of these products is accompanied by the evolution of only very small quantities of hydrogen sulphide, so that obviously the compounds formed are still essentially addition products. Even if it could be shown that these very small quantities of hydrogen sulphide were essentially due to the action of the sulphur upon the polyprene,

this would not in the least vitiate my above stated conception of the intrinsic nature of the vulcanisation process, as, in the extreme conditions under which these highly sulphuretted bodies are produced, substitution of sulphur for hydrogen is to be expected as a matter of course. Indeed, it is a matter for surprise that this secondary reaction should take place to such an insignificant extent only as appears to be the case.

It may be taken, therefore, that these products represent the upper limit of the normal reaction (addition) of polyprene and sulphur, and it is a matter of considerable interest to ascertain the numerical value of this limit. For this purpose three intimate mixtures of fine Pará and pure sulphur [1] were prepared :—

1. 100 grms. technically pure fine Pará,
   50 ,, sulphur,
   Vulcanised : 12 hours at 138° C.
2. 100 grms. technically pure fine Pará,
   75 ,, sulphur,
   Vulcanised : 9 hours at 140° C.
3. 100 grms. technically pure fine Pará,
   100 ,, sulphur,
   Vulcanised : 8 hours at 140° C.

All three samples were excellent specimens of ebonite, free from porosity, and of remarkable strength. No. 1 was comparatively the softest of the three, No. 3 being extremely hard without being brittle.

Under the microscope all three show much the same appearance of an almost structureless mass, exhibiting no recognisable differentiation (fig. 8, Plate I.).

This becomes even more distinct by examining these specimens in the state of an extremely fine dust (fig. 9, Plate I.), which is obtained by working them with a file and passing the dust thus obtained through very fine silk gauze.

On extracting these products, in the state of an impalpably fine powder, with acetone or carbon bisulphide, an extract is obtained consisting chiefly of sulphur and a very small quantity of organic matter. To completely extract the *free sulphur* contained in these samples is, however, a surprisingly slow process requiring several days' treatment in spite of the extremely fine subdivision of the substance. It is further curious that there is no difference in the rate at which the extraction proceeds in using carbon bisulphide instead of acetone—in fact, the latter, on the whole, is the more satisfactory solvent. I take this as proof that the *free sulphur* in vulcanite is present as amorphous (colloidal) sulphur insoluble in the solvents for sulphur. Under the influence of the boiling solvents a gradual reversion of this insoluble amorphous modification into the soluble crystalline form takes place, so that the rate of extraction does not depend so much upon the nature of the solvent as upon the rate of reversion of the sulphur.

[1] Precipitated with hydrochloric acid from a solution of calcium tetrasulphide.

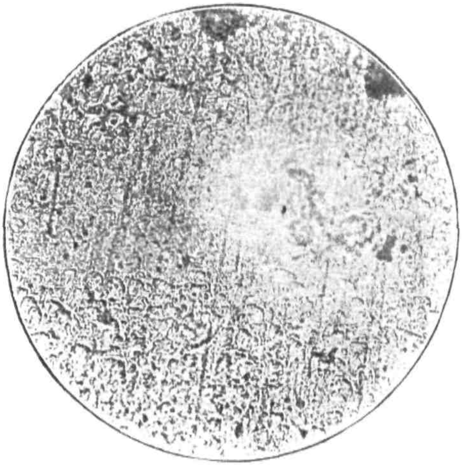


FIG. 8.—Micro-section of vulcanite (ebonite).
Photo-micrograph: Apochrom. Zeiss 4 mm., Projec. Eyep. 4. × 600.

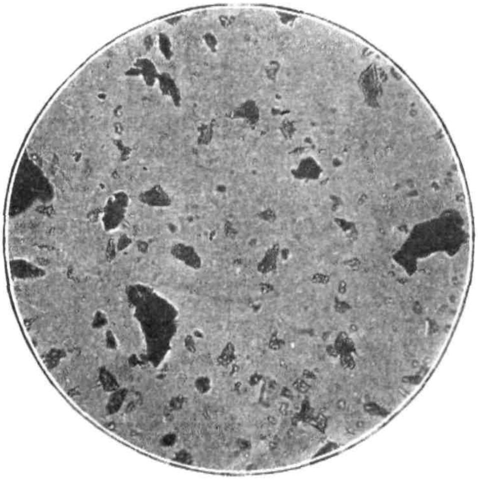


FIG. 9.—Vulcanite powder.
Photo-micrograph: Apochrom. Zeiss 4 mm., Projec. Eyep. 4. × 600.

The amount of organic matter extracted is very slight, amounting to less than 2 per cent. in all the three samples.

The samples were extracted until a full day's further extraction produced no appreciable increase in the amount of free sulphur removed. They were then dried, and the *combined sulphur* in them estimated by CARIUS' process.

The following are the results obtained :—

Sample	I.	33·08 per cent. of *combined sulphur.*
,,	II.	33·11 ,, ,, ,,
,,	III.	32·64 ,, ,, ,,

These figures quite satisfactorily approximate to the theoretical amount of sulphur in polyprene disulphide, $C_{10}H_{16}S_2 = 32{\cdot}00$ per cent. S. It is rather curious that the amount of sulphur ascertained approaches the theoretical amount the more closely, the shorter the time the sample has been heated, and the larger the amount of sulphur with which it had been mixed. I am inclined to think that this is not accidental, but points to the fact that substitution takes place after, or towards the end of, the addition process. Whether it is the india rubber constituent itself, or the insoluble constituent, which is thus acted upon, I have not been able to decide. If the vulcanisation treatment of the above samples is considerably prolonged, products are obtained in which the combined sulphur gradually, but very slowly, increases. Under these conditions the evolution of hydrogen sulphide becomes more marked as time goes on, but, at the same time, the vulcanisation products deteriorate very rapidly in quality. Their colour changes more and more into a greyish-brown, they lose their strength and hardness, and become very porous, and finally almost friable. Even in products of this description I only once observed 38·18 per cent. of sulphur.

It appears, therefore, that the sulphur addition of india rubber has reached its upper limit with the formation of a polyprene disulphide, $C_{10}H_{16}S_2$, containing 32·00 per cent. of sulphur. There must, of course, be a lower limit, below which we cannot go without leaving some of the rubber in the unvulcanised state. What this limit is we cannot ascertain at present, as we possess no means for isolating any of the terms of the series of sulphides lying within these two limits, nor for separating any of them from unvulcanised india rubber.

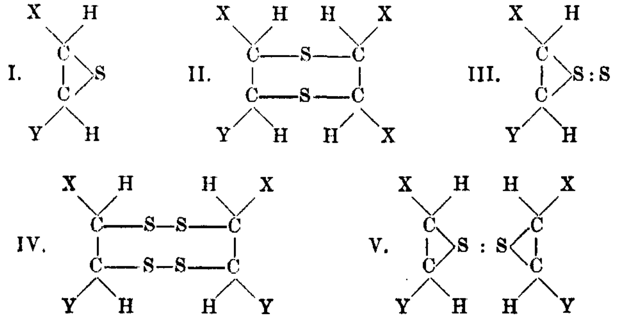
In view of the circumstance, however, that the important change produced by vulcanisation in the production of soft rubber goods becomes first clearly apparent when the vulcanised india rubber contains from 2 to 2·5 per cent. of sulphur, we may assume that this represents the lowest limit of the possible polyprene sulphides. Accepting this hypothesis, we find, by a simple calculation, that this corresponds to a compound $(C_{10}H_{16})_{10}S$, or $C_{100}H_{160}S$, so that the polyprene disulphide we recognised above in the specimens of hard rubber would be $C_{100}H_{160}S_{20}$. A compound $C_{100}H_{160}S$ would contain 2·35 per cent. of sulphur, and it is rather remarkable that

this figure should come so well within the limits observable in well-cured rubber goods possessing the highest degree of elasticity and distensibility combined with the highest degree of tensile strength. India rubber possessing a higher coefficient of vulcanisation may and does show even higher tensile strength, but at the expense of the other physical constants.

HENRIQUES states that he observed perfectly vulcanised specimens of india rubber containing less than 1 per cent. of combined sulphur, but while I do not doubt that he examined such specimens, I feel compelled to controvert most emphatically the statement they were 'perfectly vulcanised.' He gives no data in relation to their physical constants to justify the acceptance of his assurance. Throughout my experience in manufacture and analysis I have never met with a rubber sample containing less than 1 per cent. of combined sulphur which could have been described as perfectly vulcanised. It is, of course, quite possible that the technical effect describable as 'perfect vulcanisation' does not bear the simple quantitative relation to the chemical aspect of the problem which I tentatively attribute to it. In this case it would follow that the lower limit of the sulphur addition to india rubber would be still lower than I hypothetically assumed it to be, with the result that the above named molecular weight of india rubber would be still higher. But even in this case it could only be a multiple of $C_{100}H_{160}$. We are therefore now in a position to state the process of vulcanisation as follows:—

3. *The process of vulcanisation consists in the formation of a continuous series of addition products of polyprene and sulphur, with probably a polyprene sulphide $C_{100}H_{160}S$ as the lower, and $C_{100}H_{160}S_{20}$ as the upper, limit of the series. Physically this series is characterised by the decrease of distensibility, and the increase of rigidity, from the lower to the upper limit. Which term of the above series—i.e., which degree of vulcanisation—is produced is in every case only a function of temperature, time, and proportion of sulphur present.*

Respecting the configuration of any of the terms of this series, all is surmise, but the following possibilities exist:—



These diagrams show only one of the ethylene bonds known to exist in

the polyprene complex, groups X and Y representing the rest of this complex. It will be seen that for a polyprene complex $C_{100}H_{160}$, only configurations I. and II. would be possible if the lower limit of vulcanisation is expressed by the composition of a compound containing 2·29 per cent. of sulphur—that is, by $C_{100}H_{160}S$. In this case, but with the configurations shown in the diagrams III. and IV., the polyprene molecule would require doubling. Whether any, and if so which, of these diagrams represent the constitutional configuration of india rubber, only further investigation of the subject can decide.

There is one fact, well known to all rubber manufacturers, which seems to suggest rather strongly that there is, indeed, no definite relation at all between the quantitative chemical result and the physical technical effect of the vulcanisation process, inasmuch as the same degree of vulcanisation in the same kind of india rubber need not result in the formation of physically identical vulcanisation products. In other words, the fact that two different specimens of vulcanised india rubber, produced from the same brand, even from the same batch of crude rubber, possess equal amounts of combined sulphur—*i.e.*, equal coefficients of vulcanisation—by no means implies that these two specimens also possess the same physical constants, the same technical properties. It is well known that not only may two such specimens differ very widely in this respect, but it may further happen that while one of them is a practically permanently sound product, the other very rapidly deteriorates. It is, no doubt, owing to this fact that many practical rubber workers still refuse to look upon vulcanisation as an essentially chemical process, but go as far as to roundly deny it, and attempt to explain the vulcanisation phenomena as due in one part to the action of heat upon india rubber, in the other part to the mere physical penetration of the india rubber by the sulphur.

This fact is not lightly to be dismissed—indeed, it is the direct cause for the great number of conflicting statements put forward at various times by different writers, it is responsible for the very confused state of our present day views on 'the nature' of vulcanisation, and lies at the bottom of all the well-recognised technical difficulties of the vulcanisation process. Amongst the various observations bearing upon this fact the most important are as follows:—

I. Long continued working between mixing rollers destroys the resiliency of the india rubber, rendering it more and more plastic. In this state the india rubber is known to require much more sulphur for vulcanising than if it is only worked sufficiently long to mix it homogeneously with the sulphur and such other admixtures as it is desired to employ.

II. The different modes of carrying out the process of hot vulcanisation, even if performed in every case at the same temperature, produce very different results in one and the same mixing. Thus it is very well known in practice that the methods known as dry heat curing, steam curing,

press curing, hot-water curing, or curing in a sulphur bath, are by no means interchangeable processes for one particular mixing.

III. The results of quick vulcanisation at a high temperature with a large excess of sulphur, slow vulcanisation at a moderate temperature, or gradual vulcanisation in a temperature gradually rising to a maximum in the course of a very long time, even if the operations be so conducted as to produce in every case the same degree of vulcanisation, produce physically very different products.

IV. India rubber which has been rendered plastic ('killed') by much prolonged working, and exhibits the vulcanising characteristics described above (I.), on long keeping gradually loses these characteristics and reverts towards the character of moderately worked india rubber. As it does so, it also recovers largely its former resiliency, and loses the plasticity characterising its 'fatigued' condition.

The above instances comprise the most important of the physical facts influencing the physical result of the vulcanisation process, but the most remarkable point is that none of them has the least influence upon the chemical result of the process, or upon the coefficient of vulcanisation. This, as already stated, is only dependent upon the same factors which determine the rate of progress of every chemical reaction—temperature, time, and mass. In other words, whether india rubber containing a certain amount of sulphur be only moderately worked, or whether it be overworked (fatigued), or by whichever method it be vulcanised, as long as the time and temperature of vulcanisation are the same, the chemical result, the coefficient of vulcanisation, is in every case also the same, though the physical results may, and do differ, often very widely. Thus, in order to produce a vulcanisation product containing 3 per cent. of combined sulphur in a fatigued rubber mixing requires, as a matter of fact, no more sulphur than what will produce the same result in the same, but only moderately worked, mixing. But, in order to obtain the same physical vulcanisation result in the first as in the second case, a much higher coefficient of vulcanisation, and therefore correspondingly more sulphur, is needed.

The clear recognition of these facts is a matter of the highest scientific and technical importance. It enables us at once to co-ordinate and reduce to order the whole of the chaotic jumble of empirical facts in relation to vulcanisation which up to now surround the practice of the process with quite a mystic halo. The above instanced relations between the chemical and the physical effects of vulcanisation demonstrate in the most unmistakable manner that the process of vulcanisation—*i.e.*, the process of the combination of sulphur with polyprene—as a chemical reaction, proceeds independently of the physical condition or configuration of the india rubber colloid, but the physical constants of the vulcanisation product depend to a large extent upon the particular physical state of the india rubber colloid induced by the conditions under which vulcanisation was

carried out. The vulcanising process is therefore a means by which we are in a position to perpetuate any physical state to which the india rubber colloid may be brought within the conditions required for the combination of sulphur and polyprene. Or, somewhat more briefly:—

4. *As a chemical reaction the vulcanisation process is not influenced by the physical state of the india rubber colloid; but the physical state of the india rubber colloid, while under vulcanisation, largely determines the physical constants of the vulcanisation product.*

This brief sentence contains the explanation for the often apparently so utterly erratic and unaccountable behaviour of india rubber under vulcanisation, as judged by the vulcanisation products.

A most striking illustration of the correctness of the above proposition is furnished by the behaviour of recovered india rubber. In the chapter on india rubber substitutes I have pointed out that there is no recovered rubber which could be described as 'devulcanised' india rubber, that all the recovery processes can aim at and achieve is the restitution of more or less perfect plasticity in the once vulcanised india rubber colloid. I have further pointed out that there is no necessity whatever to aim at the devulcanisation of the india rubber, that this needless aim was due to an altogether erroneous conception of the nature of the india rubber colloid, and of the process of vulcanisation. It is the presence of free ethylene bonds in the india rubber which renders vulcanisation possible, and as in all soft rubber goods only one or two at most out of thirty ethylene bonds[1] can be occupied by sulphur, it is obvious that recovered soft rubber must be capable of revulcanisation, or, rather, of repeated vulcanisation. This is even true of ground soft vulcanised rubber, but in this case, fully in accordance with the above statement (4), as the physical state of the rubber in this case is that of a more or less dry cohesionless powder, revulcanisation, the actual taking place of which can easily be proved analytically, cannot produce a coherent solid unless the vulcanisation conditions be such as to produce a fusing of the powder, and therefore a cementation of its grains into one plastic mass. In the latter case this plastic condition is then the physical state in which vulcanisation takes place, which in this case, therefore, results in the formation of a coherent solid. This is clearly the reason why the employment of 'rubber dust' in the manufacture of ebonite yields such surprisingly good results, as the much higher vulcanisation temperatures applicable in this case are so much more favourable to the formation of a continuous rubber plasma by cementation due to fusion.

Now, in the manufacture of recovered rubber the object to be aimed at is not simply to leave this cementation to occur at the vulcanisation temperature as best it may, but to predetermine it. This is the reason why fixed solvents, notably mineral oils, must be present in every revulcanisable recovered rubber. The effect of these fixed solvents is to

[1] The truth of this statement, as will readily be seen, is independent of the question of the molecular weight of india rubber.

produce at very moderate temperatures continuous, and more or less already homogeneous, rubber plasmata. In this physical state, vulcanisation supervening, the result is a coherent, continuous solid which in many cases is indistinguishable from similar products made from new rubber. The vulcanised product will be found the more satisfactory, the more easily the recovered rubber used reassumes, at vulcanisation temperatures, the state of a continuous plastic colloid. If we take any brand of recovered rubber and free it from its oil by extraction with acetone, it forms, after drying, an inelastic, almost friable mass. If we mix this with sulphur and attempt to vulcanise it, the result is invariably disappointing. That vulcanisation has taken place, analysis of the product will readily show; but the oily solvent having been abstracted, the particles of vulcanised india rubber were unable to assume the physical condition necessary, in accordance with the above fourth proposition, to ensure a physically satisfactory vulcanisation product.

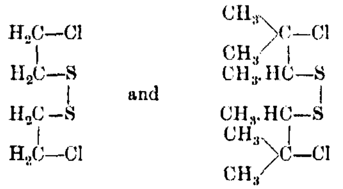
For theoretical reasons I am inclined to think that this proposition (4) applies, not only to the vulcanisation process of india rubber, but, *mutatis mutandis*, to all derivatives of all colloidal substances, the formation of which does not involve the cessation of their colloidal state, or an essential alteration of their ultimate structure or constitution.

On page 32 I have already stated that polyprene tetrabromide is generally obtained as a body forming a colloidal solution in chloroform, but insoluble in benzene and all other solvents; that in one case a product insoluble even in chloroform was obtained; in another case, however, a product, not only soluble in chloroform, but also freely soluble in benzene, resulted. The chemical composition of these compounds was exactly the same in every case, so that these physical differences are very difficult to account for. But I think that there is little doubt that they will find their explanation in the generalisation expressed in the above fourth proposition.

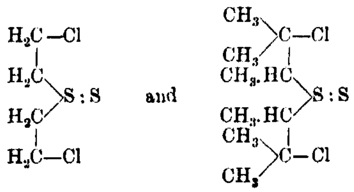
Of course it is quite possible that there may be found eventually a concurrent chemical explanation. It is well known that variations of temperature have a determining influence upon the formation of isomeric substitution derivatives. Scores of examples of this influence may be found amongst the isomeric halogen and nitro derivatives of all the aromatic hydrocarbons. The cases are comparatively rare of such an influence of different physical conditions upon substitution products, but a certain number of such cases have been observed. Considering the large number of ethylene bonds in the polyprene molecule, it is highly probable that, under varying physical conditions, the sulphur addition characterising the vulcanisation process might take effect in different places of the polyprene molecule, leading thereby to the formation of isomeric polyprene sulphides. But it has yet to be proved that in such enormous molecular aggregates isomerism of this order tangibly affects the physical properties of the compounds. The fact that, in spite of numerous attempts, not the

slightest evidence has been obtained that the Pará polyprene differs from the polyprene of any of the other numerous brands of india rubber rather points this way, as the great technical difference between them cannot be understood on any other assumption. Further investigation of this important point is urgently required, but it will be noticed that the results of such investigation could not affect our above fourth proposition, the peculiar differences between the polyprene tetrabromides, above alluded to, not being capable of explanation on the supposition of isomerism.

Vulcanisation with chloride of sulphur in the cold offers an exact parallel to vulcanisation with sulphur at higher temperatures. In an investigation of this subject[1] I showed, some years ago, that the vulcanisation with chloride of sulphur is an addition process. The action of sulphur monochloride upon unsaturated hydrocarbons was many years ago investigated by GUTHRIE,[2] who obtained the addition products ethylene chlorosulphide $(C_2H_4)_2S_2Cl_2$ and amylene chlorosulphide $(C_5H_{10})_2S_2Cl_2$. These chlorosulphides are saturated substances, and, according to these formulæ, would have the constitution,



assuming the constitution of sulphur monochloride to be Cl—S—S—Cl. More recent investigations, however, tend to show that the constitution of sulphur monochloride must be expressed by the formula $Cl_2=S:S$.[3] GUTHRIE's addition products would have to be formulated thus :—



[1] "On the Vulcanisation of India Rubber," *Journ. Soc. Chem. Ind.*, 1894.

[2] *Ann. Chem.*, 113, 270.

[3] HENRIQUES,* by the action of sulphur monochloride upon β-naphthol, obtained the following bodies :—

$HO.C_{10}H_6—S—C_{10}H_6.OH$	dioxy-dinaphtyl-sulphide, . .	M.P. 211° C.
$HO.C_{10}H_6—S—S—C_{10}H_6.OH$	dioxy-dinaphtyl-disulphide, .	M.P. 166° C.
$S:S.C_{10}H_6.OH$ / | / $S:S.C_{10}H_6.OH$	dithio-dioxy-dinaphtyl-disulphide,	M.P. 141° C.

The first of these is the chief product of the reaction, and its constitution strongly suggests that the formula of sulphur monochloride is to be expressed by $S:SCl_2$, and not

* *Ber.*, xxvii. p. 2993.

The difference for our purposes is rather insignificant, the main fact remaining that this addition process results in the formation of saturated compounds.

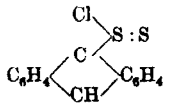
Assuming that the above compounds are typical of the interaction of sulphur monochloride with doubly linked carbon atoms, we are justified in assuming that the action of sulphur monochloride upon polyprene proceeds on analogous lines. But the reaction between these two substances is so violent, that comparatively dilute solutions should be employed, and it is also necessary to take care that only india rubber previously freed from its insoluble constituent in the manner described on page 7 is used.

The benzene serving as a solvent in these investigations should be deprived of every trace of moisture by distillation over metallic sodium. These precautions are necessary, as solutions of sulphur monochloride are very rapidly decomposed by moist solvents, and also because the action of sulphur monochloride upon the insoluble constituent of india rubber gives rise to the formation of by-products, which, if not recognised as such, would almost certainly vitiate our conclusions.

If, observing the above precautions, we prepare a 5 per cent. solution of *india rubber in benzene and add to it an excess of sulphur monochloride* also dissolved in benzene, the temperature rapidly rises, and within a few seconds the solution is transformed into a firm, very transparent jelly. The reaction is not accompanied by evolution of hydrochloric acid. The product is allowed to stand for about twenty minutes; it is then placed in a bag of fine but strong muslin, immersed in pure benzene, and the jelly squeezed through the meshes of the fabric. This is not a particularly agreeable operation, but as the product is absolutely insoluble in all solvents, it is the only means of reducing it to a satisfactory condition for further purification. It is now obtained in the state of a mass of extremely fine flakes, which are washed with benzene until every trace of the excess of sulphur monochloride has disappeared. After this it is filtered, pressed between filter paper, without previous drying transferred to a **Soxhlet**

by Cl—S—S—Cl. The same observation applies to the third of these substances. The constitution of the second body at first sight appears to suggest a reaction, which could only be satisfactorily expressed by the adoption of the symmetrical formula for sulphur monochloride. But it will readily be seen that the third compound, by elimination of sulphur, must form the second of these bodies. The evidence of this investigation is therefore strongly in favour of the asymmetrical formula for sulphur monochloride.

The observations recently made by LIPPMANN and POLLAK * on the action of sulphur monochloride upon anthracene lead to the same conclusion. The product of this reaction, anthracene di-thiochloride, appears to possess the constitution,



which also supports the asymmetrical formula of sulphur monochloride.

* *Ber.*, xxxiv. p. 2767.

extractor, and extracted with acetone until all soluble matter consisting entirely of sulphur has disappeared. It is then dried at a low temperature.

The dried product is obtained in the form of fine cream-coloured flakes which are very friable. The substance is insoluble in all solvents, but the coal tar hydrocarbons, chloroform, carbon bisulphide, nitrobenzene, terpenes, and ethereal oils cause it to become transparent and to swell more or less considerably. On heating it to temperatures above 140° C. with mesitylene, cumene, cymene, or nitrobenzene, solution, accompanied by evolution of hydrochloric acid, takes place, the product being decomposed. In the dry state this decomposition already begins at 80° C.

On suspending this product in carbon bisulphide, and treating it with a solution of bromine in the same solvent, no absorption of bromine takes place. The product behaves, therefore, as a saturated compound.

On analysis it gave the following figures:—

	I.	II.	Calculated for $C_{10}H_{16}S_2Cl_2$.
C, ...	43·61	43·51	44·28
H, ...	6·21	6·14	5·90
S, ...	23·88	23·81	23·62
Cl, ...	25·97	26·11	26·19

These figures prove conclusively that—

5. *The product of the interaction of polyprene and sulphur monochloride results in the formation of an addition product of these two compounds, possessing the empirical formula* $C_{10}H_{16}S_2Cl_2$.

The composition of this polyprene chlorosulphide is not affected by preparing it in the presence of an excess of sulphur monochloride of varying amount. In decreasing the proportion of chloride of sulphur, the reaction proceeds much as before, the time within which the beginning of the reaction, indicated by the mixed solutions becoming first stringy, then gelatinous, lengthens quite inappreciably even when so low a proportion as 5 parts of sulphur monochloride to 100 parts of polyprene is used. But the time in which the jellies formed reach their respective maximum stiffness gradually increases as the proportion of chloride of sulphur used grows less.

Provided the strength of the polyprene solution and that of the sulphur monochloride remains constant—say, 5 per cent. in both cases—the length of time that elapses before the first appearance of gelatinising (pectinising) in the reacting mixtures varies not more than about ten minutes between the limits of 120 and 5 parts of total sulphur monochloride reacting upon 100 parts of polyprene.

With increasing dilution the rate at which the reaction proceeds slackens considerably, though the final result remains thereby unaffected.

If the concentration of the polyprene solution falls to 0·5 per cent., even an excess of sulphur monochloride will only produce a peculiar 'stringy' jelly. Polyprene solutions of 0·25 per cent. strength remain apparently unaltered; whether in this case also polyprene chlorosulphide is formed or not, I have not yet been able to ascertain.

The action of sulphur monochloride upon the insoluble constituent of india rubber is distinct, but not characterised by the formation of any tangible compound. It should, however, be mentioned that it is accompanied by a very marked evolution of hydrochloric acid.

It has already been stated that the compound $C_{10}H_{16}S_2Cl_2$, the product formed by the addition of 132 parts of polyprene and 135 parts of sulphur monochloride, forms a brittle, friable mass. As we reduce the proportion of the latter, the products formed lose their friability; they become tougher, merging by gradual, imperceptible degrees into more and more resilient and distensible masses. Characteristic of the whole series of products thus obtainable is the fact that they all contain sulphur and chlorine in exactly equimolecular proportions. In other words, they are all addition products of polyprene and sulphur monochloride. They also all appear to be perfectly homogeneous products, but it is obvious that whether this homogeneity is not apparent rather than real must be decided by special experiment.

For this purpose[1] 5 grms. of pure Pará rubber were dissolved in 1000 c.c. of pure benzene, and 5·1 grms. of sulphur monochloride were added. In consequence of the great dilution, the reaction proceeded but slowly. As soon as the solution had assumed the condition of a semi-liquid stringy jelly, it was divided into two parts, the first of which was proceeded with in the above described manner. To the second part a solution of 20 grms. of Pará in 200 grms. of benzene was added, and the whole vigorously stirred, when it assumed almost the condition of an ordinary rubber solution. This solution was poured into absolute alcohol, when a voluminous, somewhat stringy precipitate was obtained. This was filtered off, the filter residue washed, and finally dried in vacuo.

The product of the first portion was, on analysis, at once found to be identical with our polyprene chlorosulphide $C_{10}H_{16}S_2Cl_2$. The dry second product formed a rather elastic, somewhat tacky mass, which, on analysis, was found to contain 4·88 per cent. of sulphur and 5·32 per cent. of chlorine. It contained, therefore, sulphur and chlorine in equimolecular proportions, and was, in this respect, indistinguishable from the product obtainable by adding to a solution of 100 grms. of Pará 11·42 grms. of sulphur monochloride.

If now we treat this substance with benzene, we obtain, in the course of a few days' standing, interrupted by frequent shaking, a slightly turbid solution, which, after considerable dilution, may be filtered through fine

[1] This is practically a repetition, quite recently made, of the experiment described in my paper already alluded to in *Journ. Chem. Soc.*, 1894.

cambric on a hot-water funnel. A fine clear filtrate is thus obtained. On the filter remains a finely distributed residue, which, after repeated washings with warm benzene, was dried. It was thus obtained as a whitish non-coherent mass, which, on analysis, was found to contain 23·46 per cent. of sulphur and 25·62 per cent. of chlorine. This substance was therefore unquestionably our chlorosulphide $C_{10}H_{16}S_2Cl_2$. It follows, therefore, that the substance containing 4·88 per cent. of sulphur and 5·32 per cent. of chlorine, out of which it was obtained, was simply a mixture of this chlorosulphide and free india rubber.

But if we now take the substance obtained by the direct interaction of 100 grms. of Pará and 11·42 grms. of sulphur monochloride, the chemical constants of which are exactly the same, and treat it with benzene, we find that although the product swells considerably, not a trace of india rubber passes into solution; so that, while this product may or may not be a homogeneous substance, it certainly does not contain any unvulcanised india rubber. Its elasticity is much greater than that of the above described mixture, and its stickiness very much less marked.

But if a product with only 11·42 grms. of sulphur monochloride pro 100 grms. of polyprene does not contain any free polyprene, it is quite obvious that between this product and the product $C_{10}H_{16}S_2Cl_2$ there must exist a whole series of intermediate chlorosulphides, and that, in reality, the compound $C_{10}H_{16}S_2Cl_2$ represents simply the upper limit of this series, exactly corresponding to the upper limit, $C_{10}H_{16}S_2$, in the polyprene sulphide series.

In my paper, already quoted, on the vulcanisation of india rubber with sulphur monochloride I have shown that a product containing 4·26 per cent. of sulphur and 4·71 per cent. of chlorine—or, say, 9 per cent. of S_2Cl_2 — and therefore closely approximating in its composition to the statistical formula $(C_{10}H_{16})_{10}S_2Cl_2$, or $C_{100}H_{160}S_2Cl_2$, does not contain any uncombined polyprene; and from this fact I drew the conclusion that the polyprene molecule could not be less than $C_{50}H_{80}$, and that it might possibly be found to be still higher.

Whether this body, $C_{100}H_{160}S_2Cl_2$, is really a homogeneous compound remains to be proved, but for the purpose of our argument the question is comparatively irrelevant. The mere fact, demonstrated by experiment, that this body contains no free polyprene is in itself sufficient proof that its molecule cannot be expressed by any smaller formula than $C_{100}H_{160}S_2Cl_2$. But the existence of such a body is entirely sufficient to draw the following conclusion :—

6. *The process of vulcanisation with sulphur monochloride consists in the formation of a continuous series of addition products of polyprene and sulphur monochloride, with a polyprene chlorosulphide $C_{10}H_{16}S_2Cl_2$ as the upper, and a compound $C_{100}H_{160}S_2Cl_2$ as the lower limit, as far as at present ascertained, of the series. Physically this series is characterised by the decrease*

of distensibility and the increase of rigidity from the lower to the upper limit.

It will be seen that this conclusion is a perfect parallel to the third of our conclusions arrived at respecting the process of vulcanisation with sulphur.

The difficulty of locating the lower limit of the chlorosulphide series with a more satisfactory degree of accuracy appears to be rather physical than chemical, as will be seen from the following experiment.

Nine grms of pure Pará were dissolved in 200 c.c. of absolutely dry benzene. To this solution was added 0·144 grm. (= 1·6 %) of S_2Cl dissolved in 10 c.c. of carbon bisulphide. The whole was violently agitated and allowed to stand for twelve hours in a dry atmosphere. At the end of this time the mass formed a stringy jelly, which could only with difficulty be distributed in 1000 c.c. of benzene. Part of this jelly passed into solution, the rest remained suspended in the solvent as an exceedingly tender colloidal sponge. The solution was separated by decantation from the latter, which was further treated with benzene. In attempting to repeat this operation until this sponge, the supposed lowest member of the above named chlorosulphide series, yielded no more india rubber to the solvent, it was found that this colloidal sponge gradually dissolved, and eventually altogether disappeared. It was then found that already the first treatment of the jelly with benzene yielded a solution containing combined chlorine and sulphur very nearly in the proportions in which these, in the form of S_2Cl_2, had been added to the india rubber. Further, on carrying the washing process with benzene just short of the complete solution of the above mentioned colloidal sponge, removing the latter as carefully as possible from the surrounding solution, and coagulating it by means of absolute alcohol, the india rubber colloid thus obtained contained only mere traces of sulphur and chlorine. We would have to assume, therefore, either that the jelly prepared as stated contained no free india rubber, and that the chlorosulphide it represents is soluble in benzene, or that the lowest possible chlorosulphide of polyprene is soluble in rubber solutions. Of these two conclusions I prefer the last one, as we have no tangible evidence on which to adopt the former, whereas the latter is not only feasible, but is, indeed, only what we should expect when forming within colloidal solutions bodies normally insoluble.[1]

The solvent action of colloidal solutions upon insoluble colloids depends, however, very much upon the concentration of the former, and ceases below a certain point. What that point is appears to depend largely upon the degree of constitutional similarity subsisting between the two colloids, so that the greater this similarity, the lower the concentration of the soluble colloid[2] necessary to keep the insoluble colloid[3] in solution. I therefore

[1] LOBRY DE BRUYN's *observations on the result of the formation of ordinarily insoluble bodies in colloidal solutions of gelatine are a case in point. See page* 77.

[2] India rubber, polyprene, in this case.

[3] Polyprene chlorosulphide in this case.

undertook a series of experiments, with the view of ascertaining as closely as possible the quantitative conditions under which a polyprene chlorosulphide is obtained which should be just insoluble in benzene or any of the other india rubber solvents.

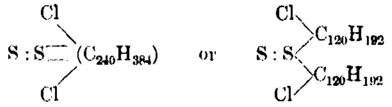
From the result of the optical investigation of polyprene, GLADSTONE and HIBBERT, in their repeatedly quoted paper, arrived at the conclusion that the smallest possible formula of india rubber had to be expressed as $C_{10}H_{16}$. This formula, indeed, agrees very well with the composition of quite a number of the derivatives of polyprene described in the foregoing pages. But in the case of polyprene iodide we were already compelled to double it, and the existence of a chlorosulphide with only 9 per cent. of S_2Cl_2 rendered it necessary to quintuple it. It should, however, be borne in mind that the proof of the homogeneous nature of this chlorosulphide is wanting, so that all it proves is that the reacting unit of polyprene cannot be less than $(C_{10}H_{16})_5 = C_{50}H_{80}$; it leaves it uncertain whether it is not perhaps $C_{60}H_{96}$ or some higher multiple of $C_{10}H_{16}$. For this reason I undertook the preparation of a series of chlorosulphides of the general formula $(C_{10}H_{16})_nS_2Cl_2$ rising from the above described chlorosulphide $(C_{50}H_{80})_2S_2Cl_2$ in increments of $(C_{10}H_{16})_2 = C_{20}H_{32}$. All the experiments were carried out with a 2 per cent. solution of very pure polyprene in benzene, to which the sulphur monochloride was added, the whole of the calculated quantity at once, in the form of a solution in carbon bisulphide containing 0·01 grm. S_2Cl_2 in 1 c.c. In every case the mixture was left standing for twelve hours, the gelatinous chlorosulphide vigorously stirred up in 1000 c.c. of benzene and allowed to stand for twelve hours with the colloidal sponge floating in it, the mass being from time to time vigorously agitated. Part of the benzene solution was then filtered off and shaken up with three times its volume of absolute alcohol, so as to precipitate every trace of polyprene present.

The result of this series of experiments is given in the following table, embodying, of course, only that part of the series approaching in either direction the critical point :—

Statistical Composition.	Percentage S_2Cl_2.	Examination of Benzene Solution.
$C_{100}H_{160}.S_2Cl_2$	9·03	Starting term of whole series. No trace of polyprene in solution.
$C_{200}H_{320}.S_2Cl_2$	4·72	No trace of polyprene in solution.
$C_{220}H_{352}.S_2Cl_2$	4·31	Very slight opalescence.
$C_{240}H_{384}.S_2Cl_2$	3·97	Distinct opalescence, but no trace of precipitate.
$C_{260}H_{416}.S_2Cl_2$	3·67	Faint but distinct precipitate.
$C_{280}H_{448}.S_2Cl_2$	3·42	Very marked, stringy precipitate.
$C_{300}H_{480}.S_2Cl_2$	3·20	Copious precipitate.

These experiments tend to show that the lower limit of the chlorosulphide series is represented by a body, the composition of which is most

probably expressed by $C_{240}H_{384}S_2Cl_2$, and that the reacting unit of polyprene, its molecular weight, must be taken either as $C_{240}H_{884}$ or $C_{120}H_{192}$, according to whether we choose to represent the mechanism of the addition of sulphur monochloride to polyprene by



The molecular weight expressed by the first of these diagrams would, indeed, be in fair agreement with the result of GLADSTONE and HIBBERT'S cyroscopic determination,[1] but this is perhaps hardly a sufficient reason to reject the second diagram with a polyprene molecule only one half that of the former, as the question of aggregation in colloidal solutions yet remains to be decided.

Incidentally also in this case attention must be drawn to the fact of the curious coincidence of the above set forth 'lower limit' with what is recognised as the best practice in manufacturing—*i.e.*, a 'cold cure' resulting in a product containing from 3·5 to 4 per cent. of sulphur monochloride in the india rubber.

We may now amend our former statement (6) by saying:—

7. *The series of chlorosulphides formed by the interaction of sulphur monochloride upon polyprene ranges from a body* $(C_{10}H_{16}S_2Cl_2)_{24} = C_{240}H_{348}S_{48}Cl_{48}$ *as the upper limit, to a body* $C_{240}H_{348}S_2Cl_2$ *as the lower limit.*

The physical behaviour of the above described colloidal polyprene-chlorosulphide 'sponges' is highly interesting. It was found to depend very largely upon the concentration of the solution in which the 'sponge' has been formed. Thus, in forming a chlorosulphide of exactly identical composition in a series of solutions of polyprene varying in concentration, we obtain a number of chlorosulphide sponges of identical chemical composition, but markedly differing in their behaviour to solvents, and also in the strength of the filaments obtainable from them on drying. This difference may be stated thus:—

8. *The greater the dilution of a solution of polyprene, the greater the tendency of the chlorosulphide formed therein to break down or disintegrate under the influence of the addition of further quantities of the solvent.*

It will be found in accordance with this that the lowest terms of the series of polyprene chlorosulphides, when formed in 0·5 per cent. solutions of polyprene in benzene, form extremely mobile jellies, which can be diluted or distended by the addition of fresh quantities of solvent, almost as readily as if they were moderately concentrated rubber solutions. Moreover, in carrying out this experiment with 0·25 per cent. solutions of polyprene, no jellies are obtained at all, nor is there even a sensible alteration in the viscosity of the solution, although the chlorosulphides are formed as

[1] *Phil. Mag.*, 1889, p. 39.

usual—a fact easily demonstrable by their precipitation with absolute alcohol and subsequent analysis.

Exactly similar observations may be made by forming chlorosulphides of identical compositions in solutions of polyprene of the same strength, but in different solvents. In treating polyprene solutions of equal concentration in different solvents with the same proportion of sulphur monochloride, jellies exhibiting surprising differences are obtained, and on subsequently drying these jellies, the tenacity of the films obtained from the different solutions varies in a remarkable degree.

That solutions of the same substance, and possessing equal degrees of concentration, may vary very considerably in their structure or constitution, or in the state of aggregation of the dissolved body, is quite a familiar phenomenon in the solutions of crystalloid substances. That it should be much more pronounced in colloidal bodies is, therefore, to be expected. Bearing this in mind, the above described phenomena become at once intelligible in the light of the important conclusion embodied in our proposition (4) on page 95.[1]

9. *The difference in the physical state of the above described solutions of polyprene after their conversion into chlorosulphides is determined by the difference of the physical conditions of the polyprene itself in different solvents, or in the same solvents at different concentrations.*

In this statement will be found the clue to all the most perplexing facts observed in the process of vulcanising with sulphur monochloride, and even of those at first sight quite unaccountable.

The indifference of polyprene to sulphur at ordinary temperatures is one of the chief causes of the difficulty of practically controlling the process, the chief advantage of vulcanisation with sulphur monochloride being the promptness of the reaction. 'Practical' workers have made this certainly striking difference the basis for some extraordinary conclusions.[2] In reality this difference is no greater than that which we find in the behaviour of unsaturated hydrocarbons with sulphur and sulphur monochloride respectively, and probably less.

As regards the action of the sulphur upon polyprene, it is perfectly obvious that the slowness of its action is due to the fact that sulphur vapours do not reach the molecular state at which their reactive energy is at its highest until very high temperatures are reached. The sulphur molecule assumes its normal density, $S_2 = 64$, only at temperatures from about 700 to 1500° C., as will be seen from the following figures :—

Bineau, ...	714 to 743° C.	D=2·7
Deville and Troost, . . .	860 to 1040° C.	D=2·13
Bineau, ...	834 to 1162° C.	D=2·36
V. Meyer, ...	1560° C.	D=2·17

[1] In all these experiments the concentration of the solutions is the gramme weight of substance contained in 100 c.c. of the solvent.

[2] See *Gummi Zeitung*, 1899, p. 17 (Höhn); *ibid.*, p. 247 (Minder).

The calculated density for the S_2 molecule is D = 2·216. The vulcanisation temperature of polyprene is necessarily much lower than the above temperatures which lie between bright red heat to white heat. The highest vulcanising temperature which has ever been proposed and used does not exceed 185° C., and in ordinary practice it is rarely more than 140° C. But at these temperatures the sulphur molecule is in a state of aggregation largely exceeding its normal value of $S_2 = 64$. Indeed, BLEIER and KOHN [1] ascertained the following values for temperatures below the boiling point of sulphur (440° C.) :—

In the Vapour of	Temperature.	Molecular Weight.	Molecular Aggregation.
Diphenylamine,	310° C.	237·9	7·43
Amyl benzoate,	262 ,,	240·1	7·50
Quinoline,	236 ,,	245·2	7·66
Ethyl benzoate,	212 ,,	249·6	7·80
Dimethylaniline,	193 ,,	251·1	7·84

These figures leave no doubt that at practical vulcanising temperatures the molecule of the sulphur vapour present differs from S_8 only by an extremely minute fraction, and as it has been shown by BECKMANN that the sulphur in solution consists of S_8 molecules only, no doubt exists that the molecule of melted (colloidal) sulphur is at least of the same order of magnitude, not improbably much larger. But as vulcanisation can only be effected by sulphur molecules S_2, it is obvious that the rate of vulcanisation *at any given temperature must be determined by the state* of dissociation of the sulphur at that temperature—*i.e.*, by the relative proportions of S_8 and S_2 molecules present. At ordinary temperatures dissociation is almost nil, hence the fact that sulphur at these temperatures cannot vulcanise india rubber, or does so to quite an unappreciable extent only. In order, therefore, to induce vulcanisation—the combination of sulphur and polyprene—we must increase the state of dissociation of the sulphur. This, as the above figures conclusively show, is effected by higher temperatures, and accordingly we find that at increasingly higher temperatures vulcanisation proceeds at a rapidly increasing rate.

The necessity for continuing the heating throughout the vulcanising operation is to be found in the circumstance that the energy consumed in the dissociation of S_8 into S_2 molecules is very high, and also that the heat of combination of polyprene sulphide is very low. Otherwise we should expect that the vulcanising reaction, once started, would proceed spontaneously without the further application of extraneous heat.

As this point can readily be proved by experiment, I considered it worth while doing so; but as the reaction between polyprene and sulphur does not lend itself to calorimetrical determinations, the more circuitous

[1] *Ber.*, 1900 [33], p. 50.

plan had to be adopted of determining the heat of combustion of polyprene, and of a polyprene sulphide of known composition, and to calculate from these data the heat of formation of polyprene sulphide.

The polyprene used in these determinations was obtained by most careful purification of specially selected Pará rubber. The polyprene sulphide used was prepared from the same lot of Pará rubber by mixing it, after thorough purification, with 10 per cent. of sulphur, vulcanising it immersed in water for two hours at 135° C., extracting all the free sulphur with acetone, and subsequently drying the product in a current of carbon dioxide at 80° C. The following figures were obtained :—

Polyprene.

Calories per Gram Water Liquid.	Molecular Combustion Heat, $C_{10}H_{16}$.	Calculated for $10C, O_2 + 8H_2O$.	Heat of Formation, $C_{10}H_{16}$.
10,669[1] *c*.	1450 *C*.	1529 *C*.	79 *C*.

Polyprene Sulphide: 3·8 per cent. S.

Calories per Gram Water Liquid.	Molecular Combustion Heat. Mol. = 141·37.	Calculated for $C_{10}H_{16}S_{0\cdot17}$.	Heat of Formation.
10,215[2] *c*.	1444 *C*.	1474 *C*.	30 *C*.

It is well known that, owing to the high combustion heat of organic substances and their low formation heat, the calculation of the latter in the above manner is apt to involve considerable error. These are, however, not of such an order of magnitude as to vitiate the above figure for the heat of formation of polyprene sulphide for the purpose of our discussion. Indeed, this figure amply suffices to demonstrate the above proposition, that the heat of formation of polyprene sulphide is low; and this, together with the energy required for the gradual transformation of the S_8 molecules into S_2 molecules, is sufficient to satisfactorily account for the indifference of polyprene to sulphur at ordinary temperatures, as also for the necessity of continuous heating during the process of vulcanising at higher temperatures.

It is incidentally interesting to compare the thermochemical data of some of the cyclical terpenes with those above given for polyprene, which we are regarding as an olefinic compound :—

Citrene.[3]

Calories per Gram.	Molecular Combustion Heat.	Calculated.	Heat of Formation.
10,959 *c*.	1490 *C*.	1529 *C*.	39 *C*.

Pinene.[3]

Calories per Gram.	Molecular Combustion Heat.	Calculated.	Heat of Formation.
10,852 *c*.	1475 *C*.	1529 *C*.	54 *C*.

[1] Mean of five determinations.
[2] Mean of three determinations; S determined as SO_3, aq.
[3] FAVRE and SILBERMANN, *Ann. chim. phys.* (3), 34, 434.

Assuming all these figures to be reliable, they reveal the curious fact that the heat of formation of these terpenes is much lower than that of polyprene. The circumstance that the last named product, on dry distillation, is almost quantitatively converted into cycloterpenes, would lead one to suppose that these, as stabler forms, would possess a higher heat of formation. This, quite apart from the fact that colloidal compounds are generally assumed to possess a higher energy content—*i.e.*, a lower heat of formation—than the corresponding crystalloids. That this, at least as a generalisation, is not correct, appears also to follow from the observation due to BERTHELOT,[1] that the conversion of soluble amorphous (colloidal) sulphur into the rhombic (octahedral) modification is accompanied by a negative temperature reaction of 160 calories per gram-molecule.

The important part played in the vulcanising process by the dissociation of the complex sulphur molecules naturally suggests the adoption of means favouring this process, either for the purpose of reducing the time or the temperature required in practical working. One device of this kind has been in practical use almost ever since the discovery of the process of vulcanisation, and consists in the use of 'sulphur carriers.' All substances to which this term applies are sulphides of the heavy metals. This statement might appear to be in opposition to the fact that lead compounds, such as litharge, lead carbonate, lead sulphide, lead chloride, lead thiosulphate, antimony oxide, are also able to act as sulphur carriers. But I contend that these compounds are capable of this action only owing to their more or less rapid conversion into sulphides under the influence of the melted sulphur and its vapours. This is strongly supported by the fact that the best of the above named sulphur carriers is lead thiosulphate, which already at water-bath temperature decomposes into lead sulphate and lead sulphide. All metallic sulphides possess a more or less pronounced tendency to form polysulphides, the vulcanising action of which has already been demonstrated by GIRARD; and the action of these sulphides, or sulphur carriers, would appear, therefore, to consist in the acceleration of the splitting up of the complex sulphur molecules. No explanation of the action of these bodies is to be obtained from the thermochemical data of the reactions in question, as the intervention of any intermediate stages in the reaction leaves the energy change of the reacting system unaffected. It is much more probable that the catalytic action of these sulphur carriers rather depends upon the matter of chemical equilibrium, and that their presence tends to render it unstable, thus hastening progress towards a lower potential, which in this case is represented by polyprene sulphide.

There is, however, another possibility of increasing the state of dissociation of the sulphur molecules, which consists in the reduction of the pressure under which the reaction (vulcanisation) takes place. We owe

[1] *Essai de Mécanique Chimique*, 1879, i. 553.

to H. Biltz[1] an exhaustive series of determinations of the density of sulphur vapour under reduced pressure at 440° C., which show to what a considerable extent the dissociation of the sulphur molecules increases under these conditions. I give the results of the observations of the above named author in the following table. I have added a third column, showing at a glance the mean atomic aggregation the sulphur vapour possesses in each case.

Pressure, mm. Mercury.	Vapour Density.	Molecule.	Pressure, mm. Mercury.	Vapour Density.	Molecule.	Pressure, mm. Mercury.	Vapour Density.	Molecule.
14·0	4·85	4·37	48·2	7·24	6·52	203·6	7·84	7·07
14·4	5·30	4·78	64·2	7·28	6·56	204·2	7·95	7·17
16·1	5·52	4·96	71·4	7·17	6·46	261·2	7·85	7·08
19·1	5·40	4·87	81·6	7·51	6·77	318·5	8·13	7·33
20·5	6·08	5·48	82·6	7·58	6·81	326·4	7·87	7·10
25·6	6·04	5·45	83·0	7·51	6·77	411·5	8·03	7·24
26·9	6·53	5·89	90·8	7·39	6·66	458·1	8·18	7·38
31·5	6·37	5·74	95·2	7·41	6·68	458·2	8·08	7·29
31·6	6·27	5·65	104·2	7·63	6·88	536·1	7·82	7·05
39·1	6·60	6·02	119·1	7·86	7·09	539·2	7·89	7·12
48·1	7·20	6·49						

From these figures it would appear that the dissociation of sulphur vapour at constant temperatures increases very considerably under the influence of reduced pressures. The suggestion of utilising this fact for the quickening of the vulcanisation process naturally occurs; and inversely, the observation of this quickening action would lend powerful support to the above pronounced theory of vulcanisation. The technical application of this suggestion is, however, out of the question, as it would invariably result in the 'blowing' of the goods treated. For this reason vulcanisation in the vast majority of cases is carried out in presses, or in pans into which live steam at from 2·5 to 5 atmospheres (38 to 75 lbs.) is admitted, or in steam-jacketed pans charged with compressed air to a pressure up to 10 atmospheres (150 lbs.). According to the above remarks, we should expect the process of vulcanisation to suffer a retardation, owing to the reduced rate of dissociation of the sulphur vapour. That this is the case there can be no doubt whatever, but this effect can be minimised by raising the temperature, and as with rising temperature the rate of progress of the vulcanisation increases much more rapidly in proportion to the retarding effect due to increased pressure, this latter drawback is not of much practical moment.

The views on vulcanisation above set forth also explain at once the fact that, in order to effect vulcanisation within a time interval satisfactory for practical purposes, we are compelled to employ what is in all cases a considerable excess of sulphur over and above the quantity entering into

[1] *Ber.*, 34, 2493.

combination with the india rubber. This excess has obviously the effect of increasing the total number of dissociated (S_2) sulphur molecules present, thereby accelerating vulcanisation, which, as is well known to all rubber manufacturers, proceeds the quicker, the larger the proportion of sulphur employed. The uncombined excess of sulphur remaining after vulcanisation in the india rubber does not crystallise on cooling, but remains distributed through its mass in extremely small globules. This can easily be demonstrated by a vulcanisation experiment under the microscope, but unfortunately I have found it impossible to produce a satisfactory photograph of this experiment. After a certain length of exposure, the vulcanised rubber is covered with a fine greyish deposit consisting of minute sulphur crystals, which in course of time become, on close examination, visible to the naked eye, and are easily seen by examining the object with a low-power microscope. In fig. 10 (Plate II.) will be seen a low-power photomicrograph of the surface of a piece of drab sheeting, showing the splendid crystallisation of sulphur on its surface. This phenomenon is technically known as '*blooming*' or sulphuring up, and is generally supposed to be due to the sulphur 'efflorescing' in some unaccountable way to the surface. The ignorance of the real state of affairs is the reason that often the most inadequate means are adopted, or the use of some quack preparation, believed to possess some occult virtue, resorted to, to prevent this efflorescence.

In order to clearly understand the nature of this phenomenon, we must examine the nature of the above mentioned sulphur globules which are present in the india rubber for some time after vulcanisation. On examining these globules under the microscope, it will be found that they have no action upon polarised light. They are therefore structureless, and do not consist of sulphur in the crystallised state. In time they crystallise, and subsequently form centres from which radiate in all directions beautiful dendritical crystals of sulphur.

These facts may be conveniently studied by producing these globules outside the india rubber by allowing sulphur vapours to deposit upon a micro cover glass. Successful preparations are easily obtained by placing in the centre of a small porcelain basin one of the metal rings used for making cells for microscopic objects. In the centre of this ring is laid a minute crystal or two of sulphur, and a cover glass deposited upon the ring. The basin so prepared is placed upon an asbestos sheet and heated from underneath with a small flame. An iridescent coating of sulphur deposits upon the under side of the cover glass, and an examination of this coating at once reveals the fact that this deposit consists of small globules of colloidal sulphur. The globules are largest in the centre; towards the periphery of the cover glass they gradually diminish in size, passing in the outermost regions below the limits of microscopic vision. The appearance of this deposit is shown in fig. 11 (Plate II.).

FIG. 10.—Efflorescence upon india rubber goods.
Photo-micrograph: Apochrom. Zeiss 16 mm., Projec. Eyep. 4. × 150.

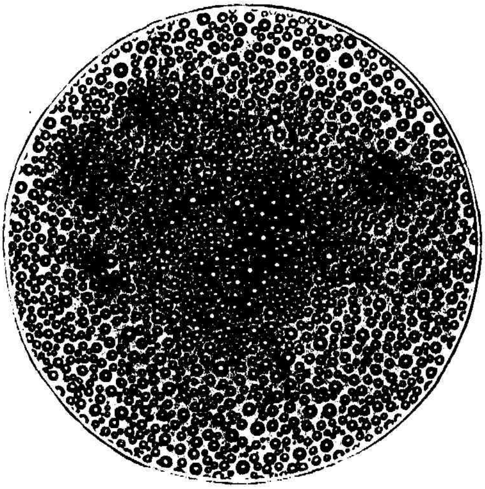


FIG. 11.—Globules of superfused (colloidal) sulphur.
Photo-micrograph: Apochrom. Zeiss 4 mm., Projec. Eyep. 4. × 600.

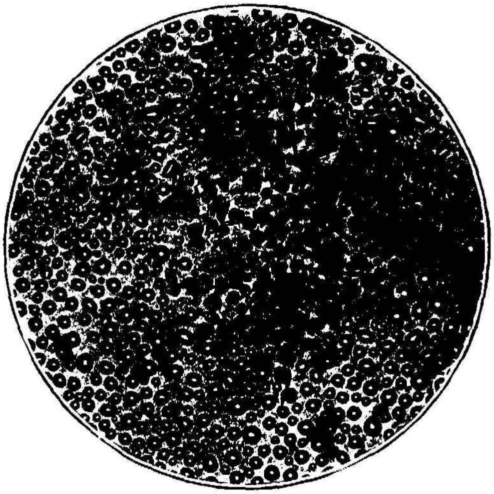


FIG. 12. Spontaneous crystallisation in deposit of sulphur globules.
Photo-micrograph: Apochrom. Zeiss 4 mm., Projec. Eyep. 4. × 600.

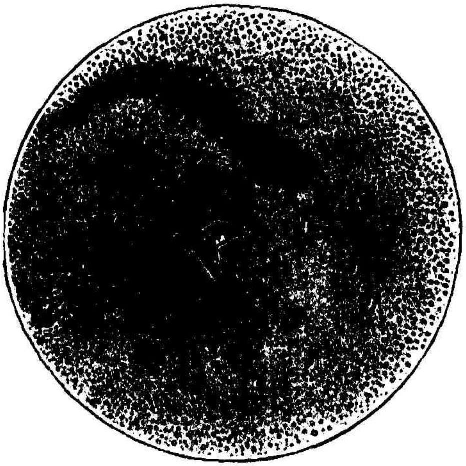


FIG. 13.—Absorption of sulphur globules by sulphur crystal.
Photo-micrograph: Apochrom. Zeiss 4 mm., Projec. Eyep. 4. × 600.

If the deposit has been produced upon a scrupulously clean cover glass, the preparation may be kept unaltered for weeks. Several times I succeeded in keeping them for such a length of time that the deposit completely volatilised without undergoing any change. As these globules consist of colloidal sulphur, they have no effect upon polarised light.

As a rule, after a few days' standing crystallisation begins at one point or another of these preparations. The first sign is always one or more of the globules becoming opaque and distinctly yellow. The crystalline structure of these globules is at once shown by the appearance of axial crosses on examining them under the micro-polariscope. The surface of these crystalline globules in course of time becomes covered with incrustations of crystallised sulphur, which often assume comparatively large dimensions, evidently at the expense of the still colloidal and brilliantly transparent globules surrounding them (fig. 12, Plate III.). This curious phenomenon is undoubtedly due to the vapour tension of colloidal sulphur being much higher than that of crystallised sulphur, so that each crystallised globule becomes a centre of low pressure, towards which, consequently, the sulphur vapours distil, to condense by crystallising. This leads to the gradual consumption of the colloidal globules by the crystallised globules surrounding them, those nearest suffering most in this respect, so that eventually the crystallised globule becomes surrounded by a zone of clear glass. All this is very clearly shown by fig. 13 (Plate III.).

Occasionally the crystalline needles forming upon a crystallised globule extend so rapidly as to make contact with one of the colloidal globules. The instant this occurs the globule becomes turbid, and almost at the same time, but always on the opposite side to that where the contact took place, a crop of extremely fine needles appears, and these making similar contact with adjacent globules, produce eventually very extraordinary dendritic designs consisting of crystallised sulphur. The following rough sketch will make the phenomena just described clear:—

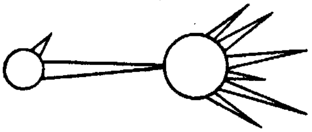


FIG. 14.—Spread of crystallisation from globule to globule in sulphur deposit.

This phenomenon is not always observable, but I have found that it can at any time be produced with perfect ease by securing the cover glass carrying the sulphur deposit upon a micro slide, so as to prevent disturbance of the sulphur deposit by contact with the slide.[1] A few drops of

[1] This is easily done by pasting across the slide two narrow strips of gummed paper at a distance somewhat less than the diameter of the cover glass. The latter, the

alcohol are run between the slide and the cover glass, when within a few seconds the above described phenomenon may be observed taking place in every direction. Fig. 15 (*see* Frontispiece) gives an idea of the magnificent dendritic designs produced, the development of which is one of the most fascinating and interesting sights conceivable. This is, no doubt, a matter deserving further careful study from the point of view of molecular physics in general.[1]

Incidentally these phenomena enable us to obtain a perfect insight into the cause and nature of the 'sulphuring up' in rubber goods—a subject which up to now has been shrouded in a great deal of mystery. It becomes at once clear that if we adopt means to start the crystallisation of the minute globules of sulphur distributed throughout the mass of the india rubber, in the inner parts of the latter no 'sulphuring up' can take place. As a matter of fact, the vapours of the colloidal sulphur globules lodging on the surface will actually travel into the rubber substance to crystallise there. But, on the other hand, should crystallisation begin upon the surface, the sulphur will pass from the colloidal globules in the inside to the surface, and produce there a frequently quite prodigious crystallisation, which is as a rule looked upon with extreme disfavour.[2]

In ebonite the trouble of 'sulphuring up' is unknown. This, in the light of the above, must appear as rather surprising, seeing that even high grades of ebonite rarely contain less than 15 per cent. of free sulphur, and often up to 60 or 70 per cent. We must therefore assume that ebonite represents a solid colloidal solution of the colloidal polyprene sulphide $C_{10}H_{16}S$ in colloidal sulphur. Nor is this assumption without experimental support. Indeed, the fact that ebonite under the microscope presents the appearance, as shown in fig. 8, of a homogeneous mass, although it contains always a large amount of free sulphur, appears to me capable of no other explanation.

The process of vulcanising with sulphur monochloride is, of course, characterised by the fact that it takes place at ordinary temperatures. Indeed, so energetic is the reaction in this case, that in employing this process, and in order to render it controllable, the sulphur monochloride must be used in a state of considerable dilution. These facts have been just as much misunderstood as those in reference to the process of vulcanising with sulphur.

At first sight it might appear strange that a compound of sulphur should

sulphur covered face downwards, is then placed upon the slide so that it rests upon these strips, upon which it is secured with two similar strips.

[1] To those interested in molecular physics, BÜTSCHLI's *Microstrukturen des erstarrten Schwefels*, Leipzig, 1900, may be strongly recommended.

[2] I have obtained similar deposits of colloidal selenium forming magnificent, highly transparent, irregularly shaped (not globular) ruby beads. These do not exhibit any of the above described phenomena—in fact, some preparations made over eighteen months ago have been preserved, and show, so far, no tendency at all to crystallise.

be such an enormously more active vulcanising agent than free sulphur itself. If polyprene and sulphur monochloride united in the vulcanising process in the manner in which the components of a double salt unite, this would at once render the process intelligible, but this is not the case. The chemical behaviour of the polyprene chlorosulphide clearly shows that the chlorine and sulphur of the monochloride separate and pass to different parts of the polyprene molecule. Now the formation of sulphur monochloride is expressed by the equation:

$$(1) \qquad S_2, Cl_2 = S_2Cl_2 + 14257 \text{ cal.},$$

and therefore its combination with polyprene involves the inverse reaction:

$$(2) \qquad S_2Cl_2 = S_2, Cl_2 - 14257 \text{ cal.},$$

or, in other words, it requires the expenditure of a considerable amount of energy.

It will be remembered that in discussing above the chemical indifference of polyprene to free sulphur at ordinary temperatures, I pointed to the fact that the dissociation of S_8 into S_2 molecules would require a considerable expenditure of energy, and that, moreover, the heat of formation of polyprene sulphide was probably very small—an assumption fully sustained by the result of the determination of that constant. It might seem, therefore, as if the circumstances were exactly the same in the case of vulcanising with sulphur monochloride. This is of course true, as far as the necessity, just pointed out, of splitting up of the S_2Cl_2 molecule is concerned; nor can the 'heat-toning,' due to the combination of the sulphur of the latter, amount to any more than in the former example.

The explanation of the energetic reaction between polyprene and sulphur monochloride is obviously to be found in the circumstance that besides the vulcanising action—the combination of S_2 with polyprene—there is a secondary reaction simultaneously taking place—the combination of Cl_2 with polyprene (addition)—and this whole process must be represented by the equation:

$$(3) \qquad (C_{10}H_{16})_n + S_2Cl_2 = (C_{10}H_{16})_nS_2Cl_2 - 14257 \text{ cal.} + (14257 + x) \text{ cal.},$$

or, in other words, the energy absorption due to the decomposition of S_2Cl_2 into S_2 and Cl_2 must be very greatly exceeded by the 'heat-toning' of that phase of the reaction expressible as

$$(4) \qquad (C_{10}H_{16})_n + Cl_2 = (C_{10}H_{16})_nCl_2,$$

i.e., by the formation of a chlorinated addition product.[1]

Now, for the final proof of the above we would require to know the formation heat of the body $(C_{10}H_{16})_nCl_2$. This constant I have not been

[1] Of course I do not mean by this that a polyprene chloride and a sulphide form side by side as separate bodies. The above only refers to the two phases in which the chlorosulphide is formed.

able to ascertain, for the simple reason that the body in question has, so far, not been obtained. Chlorine acts upon even very dilute solutions of polyprene with such violence as to lead immediately to the body $C_{10}H_{14}Cl_8$ (*see* page 31). The energy liberated in this reaction is so considerable, that in working with a 2 per cent. solution of polyprene in chloroform the latter soon begins to boil. This fact in itself is almost sufficient to prove the above conclusion—namely, that *the energy with which sulphur monochloride combines with polyprene is due to the very considerable heat-toning accompanying the combination of chlorine with polyprene.* The sulphur thereby liberated appears in what we have recognised as the most active form of S_2, the simultaneous combination of which with the polyprene produces a further addition to the total heat evolved.

Quite in accordance with the foregoing is the fact that the action of sulphur monobromide upon india rubber is very much slower than that of the monochloride. Sulphur iodide is practically without action at ordinary temperatures. The reason is evidently that the formation heat of polyprene bromide is a fraction only of that of the chloride, and the heat-toning due to the combination of iodine with polyprene is almost imperceptible.

The theory of the action of sulphur monochloride upon polyprene, given above, furnishes, moreover, an explanation of why such bodies as thionyl chloride $SOCl_2$, or sulphuryl chloride SO_2Cl_2,[1] which, from the similarity of their structure or constitution with that of sulphur monochloride, would be expected to react in a similar manner with polyprene, forming a new type of 'vulcanised' india rubber, have, as a matter of fact, not the slightest effect upon it. The explanation is as follows:—Equation (3) above contains the term $(14257+x)_2$, which represents the heat-toning due to the combination of Cl_2 with polyprene. I have given it that particular form merely to denote that this amount is x cals. larger than the energy absorption due to the splitting up of S_2Cl_2 into S_2 and Cl_2, and very little consideration will show that by the introduction into the equation (3) of either thionyl chloride or sulphuryl chloride, this term $(14257+x)$ would remain quite unaffected. The formation heat of thionyl chloride is $+40{,}800$ cals., that of sulphuryl chloride 82,540 cals. Inserting these values in equation (3), we would obtain respectively for thionyl chloride:

$$(5) \quad (C_{10}H_{16})_n + SOCl_2 = (C_{10}H_{16})_nSOCl_2 - 40800 \text{ cal.} + (14257 + x) \text{ cal.},$$

and for sulphuryl chloride:

$$(6) \quad (C_{10}H_{16})_n + SO_2Cl_2 = (C_{10}H_{16})_nSOCl_2 - 82540 \text{ cal.} + (14257 + x) \text{ cal.}$$

These two reactions to maintain the exothermic character of equation (3) would therefore require an enormous heat-toning for the combination $C_{10}H_{16}Cl_2$; and although this is considerable, approximate thermometrical

[1] Not to mention the large number of organic and inorganic acid chlorides.

observations of the reaction according to equation (3) leave no doubt that it is much too small to render equations (5) and (6) exothermic. Hence the reactions assumed in them do not take place at all.

Inversely, there is hardly any doubt that if we could find compounds of the above named type of a formation heat approximately equal to, or lower than, that of sulphur monochloride, we could obtain by means of them a reaction analogous to that expressed in equation (3). Such a compound would represent a new vulcanising agent, the discovery of which would not only be of great theoretical interest, but most likely also of considerable technical value.

CHAPTER II.

EXAMINATION AND VALUATION OF INDIA RUBBER AND GUTTA PERCHA.

WHETHER we examine india rubber or gutta percha, the first consideration is obviously how much of the pure hydrocarbon $(C_{10}H_{16})_n$ a given sample contains. Upon this point depends very largely the value of the sample, and also, though in a less degree, its suitability for a given purpose. Since, however, the pure hydrocarbons contained in the different brands of india rubber are neither physically nor chemically identical, it is evident that they cannot be technically equivalent. This fact is, as the result of technical experience, clearly expressed in the scale of prices of the different brands of india rubber, which is not so much an indication of the relative purity of these brands, as of their manufacturing value based upon their properties and applicability.

The systematic examination and valuation of india rubber is at present very little practised otherwise than by estimation of the 'loss on washing,' and it certainly must be admitted that under the conditions under which, at the present time, india rubber is bought and sold, the result of such an examination could not influence the price paid, which is determined chiefly by the state of the market, and accepted or refused by the buyer upon the strength of a cursory empirical examination of samples which are often submitted 'bulk not guaranteed.' Under these circumstances the prices paid for different lots of the same brand of india rubber, supposed to be of identical quality, often show the most absurd variations when calculated upon the yield of washed product, and after deducting from this the estimated percentage of resinous matter it invariably contains. These variations are, of course, greatest in medium and low class rubbers.

This state of affairs is highly anomalous. It could not be said to be due to the conditions under which crude rubber is collected, nor could it be considered to be a deliberate creation of the rubber broker. Indeed, there is little doubt that it is simply an old custom perpetuated by the conservatism, not to say indolence, of the rubber manufacturer, who, as a class, has done next to nothing to bring to bear upon the development of his industry that line of scientific enquiry—chemistry—which has done

more for the industrial development of this century than any other branch of human knowledge. Pig iron, caustic soda, wood pulp, and scores of similar articles, costing, comparatively speaking, a few shillings per ton, are bought and sold on the basis of strict analytical standards; but india rubber, costing from £150 to £500 per ton, changes hands without either buyer or seller having more than a vague knowledge of its intrinsic value.

But even more important is the systematic analytical control of the crude rubber before it enters into the manufacturing process. This applies more particularly to the amount of what, in the absence of more definite knowledge, is described as 'oily and resinous matter' contained in the washed rubber. The substances falling under this head exert a very marked influence upon the behaviour of the rubber in working, and also, as might be expected, upon the properties and quality of the manufactured article. As already stated, the amount of these impurities, which is slight in fine Pará, varies often rather considerably in medium and low grade rubbers; and uniformity in the manufactured article, the lack of which is so frequent a cause of trouble, cannot be expected if the most elementary precautions to attain it are neglected.

The most important points in the examination and valuation of crude rubber are:—

(*a*) Loss on washing.
(*b*) Oily and resinous matters.
(*c*) Percentage of oxygen combined with rubber.
(*d*) Ash.

The loss on washing can only be estimated in the factory by determining the yield of dry washed rubber obtained from an ascertained bulk of crude rubber. This loss consists of water, salts, wood, fibres, and mineral impurities. Of the nature of the oily and resinous substances nothing definite is known. The oily substances always form a very small part only of the total extract. The resinous substances generally form semi-transparent, yellowish-brown or brown substances, which in some cases are semi-resilient and slightly sticky, in other cases hard and brittle, and in a few cases represent white powders in appearance greatly resembling the albane extracted from gutta percha. This kind of resin, which is very difficultly soluble in all solvents hot and cold, occurs chiefly in African rubbers, most plentifully in Sierra Leone. Its composition is expressed by the formula $C_{10}H_{16}O_2$.

The estimation of these oily and resinous constituents is best carried out by drying a piece of the washed rubber either in vacuo or in a current of carbonic acid, and extracting from 5 to 10 grms. of the sample in a Soxhlet extractor by means of acetone.[1] The extraction should be continued for

[1] In some cases it may be found preferable to perform the extraction by means of glacial acetic acid, owing to the presence in a few cases, notably Sierra Leone, of resins which in acetone are scarcely soluble at all.

from six to ten hours. After distilling off the acetone, the flask with the extract is for about twenty minutes placed in a drying oven at 100° C. An air current is then blown through the flask while still hot to expel the last traces of acetone and water vapour, and finally the flask and its contents are weighed. The amount of extract thus found should be calculated upon the washed, and not upon the crude, rubber.

It is at the present time often assumed that the percentage of resinous matter in india rubber may be taken as an indication of the care bestowed upon its collection, coagulation, and preparation for the market in general. I have, however, satisfied myself that this view is not correct. A number of samples of different kinds of india rubber milk, which I had the opportunity to examine, showed that these resinous matters already exist in the milk as it flows from the trees, and much in the same proportion to the rubber present which we find in the corresponding commercial rubbers. Of course, the very fact of the existence of Spiller's resin, which body is certainly an oxidation product of the rubber itself, would seem to suggest and support the above mentioned view; but I am of opinion that the proportion of resinous matters in crude rubber due to this cause is in all but very exceptional cases extremely small. My reason for this statement lies in the fact that there must be quite a number of intermediary oxidation stages between india rubber and Spiller's resin, so that commercial india rubber containing throughout its mass a certain proportion of Spiller's resin would almost certainly exhibit such a high degree of general oxidation as to possess the properties of a more or less resilient resin rather than those of india rubber. It might perhaps appear that the above views scarcely offer an explanation of the variation of the amount of resin in the same description of india rubber—a variation which is often not inconsiderable, especially in medium and low grades. I am inclined to ascribe this variation, as far as it is *bonâ fide*, either to the condition or the age of the tree from which the latex is obtained, or to the very common indiscriminate mixing of the milks or products of good and of indifferent quality; but there is no doubt that not infrequently it may be due to deliberate adulteration practised by the collectors. The sometimes very striking qualitative variation of the resinous extract points rather strongly, I think, to the latter cause. It is, however, highly desirable that this question should be studied in a systematic manner in the various rubber districts.

The rubber, freed from oily and resinous matters by extraction with acetone, is by no means the pure hydrocarbon, but contains invariably a certain amount of oxygen derivatives of the general formula $(C_{10}H_{16})_nO_m$. From the very composition of these products I am inclined to consider them as true oxidation products (by addition) of india rubber, and I further hold that the amount of such oxygen found in india rubber is a good indication of its quality from the point of view of its collection and preparation for the market, also of its condition after shipping and storing.

The estimation of this oxygen is, of course, carried out by combustion,

the rubber obtained after extraction with acetone and drying in an atmosphere of hydrogen or carbonic acid being used for this purpose. At the end of the combustion, the weight of the ash remaining in the porcelain or platinum boat must be ascertained, and deducted from the weight of the substance used for combustion, before calculating the percentages of carbon and hydrogen in the sample. The amount of ash thus found might be supposed to represent the total amount of ash present in the washed rubber, but this is only true as an approximation. It may be taken as practically correct for all those brands of india rubber containing not more than about 4 per cent. of resin. In rubbers in which this quantity is exceeded, a certain proportion of mineral matters invariably passes into the extract—this the more, the higher the proportion of resin present. For practical purposes the amount of ash found in the boat after combustion is sufficiently near the truth; if greater accuracy is desired, it should be estimated in the washed rubber, before extraction, by incinerating in a platinum capsule.

The following tables show the mean values for the loss on washing, oily and resinous matters, oxygen, and ash of a number of different brands of india rubber.

Trade Name.	Loss on Washing.	Oils and Resins.	Oxygen.	Ash.
	%	%	%	%
Pará, hard cure,	15	2·1	1·2	0·5
,, soft ,,	17	2·5	1·4	0·3
Negro Head,	32	7·1	...	1·4
Matto-Grosso,	26	2·5	...	...
Peruvian Ball,	22	3·6	...	1·4
Cameta,	26	2·2	...	...
Ceara (Maniçoba),	32	2·0	5·4	2·74
Mangabeira,	34	6·3	1·5	...
Nicaragua Scrap,	31	5·9	6·9	5·3
Gambia,	28	7·4	...	2·4
Gaboon,	28	...	...	...
Manoh Twist,	25	7·4	4·4	0·7
Lagos,	22	4·8	2·3	0·5
Congo Ball,	28	8·0	4·0	0·8
Sierra Leone, red,	26	...	2·3	1·5
,, white,	23	...	2·1	2·1
Lopori,	12	2·8	3·9	..
Kassai, red,	8	3·8	5·5	...
,, black,	10	4·0	5·3	2·3
Angola, black,	26	...	...	...
Mozambique,	16	5·1	7·2	...
Madagascar, pinky,	20	8·4	4·2	1·8
,, black,	22	8·8	...	2·0
Assam Slabs,	24	13·7	1·4	4·3
Borneo,	48	2·2	2·58	2·2
Rangoon,	17	11·0	7·4	4·9

It should be clearly understood that the percentages figuring in the different columns of these tables are not all calculated upon the crude rubber. Indeed, this is only the case for the 'loss on washing.' The oils

and resins are calculated upon the washed rubber, the oxygen and the ash upon the washed and extracted rubber.

The 'loss on washing' of a given brand of india rubber can hardly be looked upon as an indication of its intrinsic quality. Its importance lies, of course, in the fact that its amount proportionately influences the price of the rubber in its manufacturing condition. Nor is the amount of ash found in a sample of india rubber a matter of much moment from the technological point of view, although its estimation from time to time serves as a useful check of the efficiency of the washing operation in the factory. On the other hand, the percentage of oils and resins in a given sample of india rubber has an important bearing upon its behaviour in manufacturing, and upon the quality of the manufactured goods. Generally speaking, a rubber will prove the 'softer' in working, the higher the percentage of oily and resinous matter it contains. This is roughly true for rubbers from all sources, and absolutely true for different lots of the same brand. The effect of these oils and resins is therefore invariably to facilitate the compounding and the mechanical working of the rubber in general, and for this reason their presence in rubber would not appear to be objectionable, but only becomes so in those rubbers in which the amount of these resins is liable to vary between wide limits. The objection in the latter case rests upon the fact that the resins exert a very distinct retarding effect upon the vulcanisation, and tend to produce 'shortness' in the manufactured article. The technological effect of the oxygen in the india rubber seems to have been altogether overlooked up to now. Its retarding effect upon the vulcanisation process is quite remarkable, and likewise the considerable reduction of the elasticity of the manufactured article.

A careful consideration of the above points enables us to judge in a very satisfactory manner the relative commercial value of a given sample of india rubber in reference to a standard sample of the same brand. To a certain point these determinations will also enable us to compare two samples of different brands of india rubber, but it should be well understood that they are entirely inadequate for the estimation of the intrinsic value of the pure rubber contained in one brand, as compared with the value of the pure rubber contained in another different brand of india rubber. We have seen that all the different brands of india rubber contain as chief part the same hydrocarbon (*see* page 11) $C_{10}H_{16}$, but it is, on the face of it, most improbable that this similarity should extend beyond the empirical formula. We possess no chemical evidence at the present time of any structural chemical difference between the india rubber hydrocarbons of different brands of commercial india rubber, but it is an absolute certainty, well known to every manufacturer, that the different brands of india rubber vary considerably in their behaviour under manufacturing conditions. Thus we distinguish between quick and slow vulcanising rubbers; we know from experience that certain brands of rubber form satisfactory products if vulcanised with chloride of sulphur, others do

not admit of this kind of vulcanisation. There are ranges of india rubber which experience has proved to be particularly suitable for rubber shoes, others for elastic thread, others for waterproofing, and again, others for the manufacture of ebonite.

Making full allowance for this fact that the india rubber manufacturer is practically only interested in the physical property, and takes only the slightest cognisance, if any, of the chemical side of his manufacture, it is, nevertheless, remarkable that no reaction is known at present which would allow us to differentiate any of the india rubber hydrocarbons from all the others.

The following synoptical tables, comprising all important brands of india rubber, their geographical and botanical origin, general appearance, technical and analytical constants, will be found useful for reference.

I. India Rubber Brands of South America.

Trade Name.	Geographical Origin.	Botanical Origin.	Characteristics.	Loss on Washing per cent.	Resin in Dry Washed Rubber per cent.	Ash in Dry Washed Rubber per cent.	Appreciation.
1. Fine Pará, up river, hard cure.	Amazon District, Brazils. Rio Negro. On the Tapajos and Madeira. Venezuela. British Guiana.	*Hevea braziliensis.* ,, *lutea.* ,, *spruceana.* ,, *benthamiana.* ,, *pauciflora.*	Large loaves, blackish-brown outside, inner parts light cream colour. Sections show loaves formed by concentric layers, which can be separated from each other. Empyreumatic smell.	12–18	1·3	0·3	Very strong and elastic. Standard of all rubber qualities.
2. Pará, fine island, soft cure.	As No. 1.	As No. 1.	Very similar to No. 1, but much larger loaves weighing up to 100 lbs. each. Rather softer than the foregoing.	10–15	1·3	0·5	Not quite as strong as No. 1.
3. Pará, entrefine.	As No. 1.	As No. 1.	Consists chiefly of imperfectly smoked loaves of fine Pará.	15–20	2·5	0·6	Softer than No. 1 or No. 2, and less strong.
4. Negro Heads. Sernamby.	As No. 1.	As No. 1.	Consists of a mass of lumps and shreds of all sizes, generally very dark in colour.	20–40	6·7	2·2	Lowest of Pará qualities.
5. Matto-Grosso. Virgin Rubber.	Province of Matto-Grosso, Brazils.	As No. 1.	Fairly regularly shaped pieces about 10 inches long. Straw-coloured, variegated on fresh cuts.	15–30	2·5	1·1	Good strong quality.

6. **Cameta.**	South-western Pará.	As No. 1.	Not smoked, but often deep black outside, almost pure white inside.	25–30	1·4	0·4	Rather soft, but good quality.
7. **Ceara Scraps. Maniçoba.**	Province Ceara, Brazils.	*Manihot glaziowii.*	A tangle of shreds, ribbons, and 'tears.' Amber-yellow to pale brown colour.	20–30	2·4	2·8	Strong dry rubber. Contains much wood, bark, and sand.
8. **Bahia.**	Province Bahia, Brazils.	*Hancornia?*	Large irregularly shaped lumps or slabs.	18	9·7	0·8	An excellent variety, almost as strong as Pará.
9. **Pernambuco. Mangabeira.**	Province Pernambuco, Brazils.	*Hancornia* species.	Rectangular slabs varying in size. On the outside reddish-brown, on the cut light pink.	30–40	5·9	3·1	A rather poor rubber, probably injuriously affected by coagulation of the latex with alum.
10. **Maranham. Mangabeira.**	Province Maranham, Brazils.	,,	Irregularly shaped lumps.	30–35	5·8	2·4	Rather superior to the previous brand.
11. **Bolivian Pará. Fine, medium, and niggers.**	Bolivia.	Various species of *Hevea.*	Very similar to Pará.	15	1·6	0·4	Much like Pará.
12. **Columbian. Carthagena.**	Columbia.	*Hevea* species? *Castilloa elastica.*	Very large balls or slabs. Black outside, dark grey cut.	25–50	6·7	2·8	Good qualities are much valued.
13. **Cayenne.**	French Guiana.	*Hevea* species.	In appearance much like Pará.	15–20	2·2	0·4	In quality closely approaching Pará.
14. **Guayaquil.**	Ecuador. Columbia.	*Castilloa elastica.*	Almost black surface, contains much moisture and solid impurities.	30–40	5·7	1·2	Quality very variable, often highly elastic.

I. India Rubber Brands of South America—*continued.*

Trade Name.	Geographical Origin.	Botanical Origin.	Characteristics.	Loss on Washing per cent.	Resin in Dry Washed Rubber per cent.	Ash in Dry Washed Rubber per cent.	Appreciation.
15. **Peruvian Slabs. Caucho.**	Peru.	*Hevea.*	Very dark outside, variegated porous cut.	20–30	3·6	1·4	In quality equal to second or third-rate Pará.
16. **Peruvian Ball.**	,,	,,	Large balls.	20–30	3·6	1·2	Quality as previous brand.

II. India Rubber Brands of Central America.

Trade Name.	Geographical Origin.	Botanical Origin.	Characteristics.	Loss on Washing per cent.	Resin in Dry Washed Rubber per cent.	Ash in Dry Washed Rubber per cent.	Appreciation.
17. **Panama. Costa Rica. Honduras.**	Columbia. Ecuador.	*Castilloa elastica.*	Small scraps or tears formed into balls, varying in colour.	18–30	4·4	1·5	Generally very fair qualities.
18. **Mexican Strips.**	Mexico.	,,	Dark, almost black strips; lighter inside.	30	5·3	1·1	A very strong rubber.
19. **Guatemala Sheets. West Indian Sheets.**	Guatemala.	,,	Varying in colour from black to brown.	25–35	7·2	3·0	A fair medium rubber.
20. **Nicaragua Scraps and Sheets.**	Nicaragua.	,,	Very dark, generally black.	10–15	2·8	1·1	Excellent quality, running Pará very close.

III. India Rubber Brands of Africa.

1. **Senegal Balls.**	French Senegal.	*Landolphia senegalensis.*	Balls containing much water and bark. Pink and white colour.	30–50	6·1	4·0	A strong rubber in good demand.
2. **Gambia Balls. Casamance.**	French Senegal. British Gambia. Portuguese Guinea.	As above, also: *Landolphia Heudelotii.* *L. florida.* *L. tomentosa.*	Narrow strips wound into balls.	15–30	5·5	2·6	First qualities excellent, second qualities very inferior.
3. **Sierra Leone Niggers. Massai Niggers.**	Sierra Leone.	*L. owariensis.* *L. florida.*	Reddish-brown balls, on the cut pink and glassy white.	10–25	6·8	0·4	Very good quality.
4. **Sierra Leone Twist. Manoh Twist.**	,,	As before.	Balls and lumps, rather dark outside, lighter on the cut.	20–30	6·7	0·7	Very fair quality.
5. **Liberia Balls and Flakes.**	Liberia.	?	Large balls, dark outside, grey on the cut.	15–25	5·9	1·2	,, ,,
6. **Grand Bassam. Accra. Cape Coast.**	Gold Coast.	*L. owariensis.* *L. florida.* *Kickxia africana.*	Lumps, strips, or biscuits, mostly dark in colour.	25–35	7·0	1·0	Better qualities much valued.
7. **Gaboon Balls.**	French Congo.	*L. florida.* *L. Petersiana.* *L. owariensis.*	Large and small balls, occurring in many colours.	25–35	7·3	0·9	Large balls very strong, small balls rather soft.
8. **Gaboon Strip.**	,,	As previous brand.	Colour white or grey.	35–45	11·4	1·8	Very low quality.
9. **Red Kassai.**	Congo.	?	Small mahogany-coloured balls.	·6–8	4·4	0·6	Very strong, considered the best of Congo rubbers.

III. India Rubber Brands of Africa—*continued*.

Trade Name.	Geographical Origin.	Botanical Origin.	Characteristics.	Loss on Washing per cent.	Resin in Dry Washed Rubber per cent.	Ash in Dry Washed Rubber per cent.	Appreciation.
10. Black Kassai.	Congo.	?	Small black lumps or tongues.	8–11	5·7	0·4	Less valued than the red variety.
11. Upper Congo.	,,	*Landolphia Petersiana.*	Dark brown balls.	14	7·7	0·6	A very sound, strong rubber.
12. Lopori Balls.	,,	?	Aggregates of small balls, black outside, white inside.	8–16	3·2	1·2	Very pure strong quality, much valued.
13. Equateur.	,,	?	Aggregates of small balls, dark outside, rather lighter inside.	6	3·3	0·7	Highly valued.
14. Aruwimi. Banqui. Bumba. Bussira. Lac Leopold. Mongala. Ruki. Sankuru. Yakoma.	Congo State.	?	Balls varying in size, often somewhat resembling the two previous brands. Frequently badly smelling and sticky.	up to 35	5·2	0·7	Their value varies greatly according to condition.
15. Uelle.	,,	?	Large slabs weighing from 10 to 20 lbs. Dark outside, white inside.	7	5·0	0·9	Very good medium quality.

16. Lower Congo (Thimbles). Luvituku.	Congo State. Angola.	*Carpodinus lanceolatus.* *Clitandra Henriquesiana.*	Small cubes, brown or black outside, generally brown or grey inside.	12–35	8·2	1·2	Fairly strong rubber. Dry lots very good, wet lots mostly inferior.
17. Loanda Thimbles.	Portuguese Congo. Angola.	*Landolphia owariensis.* *L. florida.* *L. Petersiana.* *L. parviflora.*	Aggregates of small balls, grey outside, light grey inside.	15–20	6·6	1·4	Has a tendency to grow soft and sticky on storing.
18. Angola Niggers.	Angola.	?	Small balls, brown outside, pinky-brown inside, almost transparent in centre.	18	9·0	0·5	A medium quality.
19. Benguela Niggers.	Angola. Benguela.	?	Small balls or sausages, reddish-brown outside and inside. Contains much bark.	20–25	4·0	0·6	Highly valued when dry.
20. Mozambique Spindles.	Mozambique.	*L. Kirkii.* *L. florida.* *L. Petersiana.*	Finger-shaped pieces. Colours yellow, pink, brown, or black.	12–20	6·4	1·3	Clean lots highly valued.
21. Mozambique Marbles.	,,	Same as No. 20.	Black or light brown small balls, reddish-brown, sometimes white inside.	12–20	7·9	2·6	Rather low quality.
22. Pinky Madagascar.	Madagascar.	*L. Madagascariensis.* *Tabernæmontana* spec.	Slabs and balls, brown outside, flesh-coloured inside.	20	7·2	0·2	Very highly valued.
23. Black Madagascar.	,,	Same as No. 22.	Large round cakes, black outside, white, pink, or buff-coloured inside.	30	10·4	1·1	Much less valued, chiefly used for hard rubber goods.

III. India Rubber Brands of Africa—*continued.*

Trade Name.	Geographical Origin.	Botanical Origin.	Characteristics.	Loss on Washing per cent.	Resin in Dry Washed Rubber per cent.	Ash in Dry Washed Rubber per cent.	Appreciation.
24. **Madagascar Niggers.**	Madagascar.	Same as No. 22.	Large dark-coloured balls, brown, white, or black inside.	25–45	7·8	2·3	Lots vary much in value.

IV. India Rubber Brands of Asia and Oceania.

Trade Name.	Geographical Origin.	Botanical Origin.	Characteristics.	Loss on Washing per cent.	Resin in Dry Washed Rubber per cent.	Ash in Dry Washed Rubber per cent.	Appreciation.
1. **Assam.**	Assam.	*Ficus elastica.*	Large slabs or balls. Inside dark red-brown, with white and pink parts.	15–40	5·6	0·7	Quality much deteriorated. Production decreasing.
2. **Rangoon.**	Burma and Annam.	*Ficus elastica.* *Urceola esculenta.* *Parameria glandulifera.*	Appearance very similar to Assam.	12–30	4·4	0·7	Quality somewhat better than Assam.
3. **Penang.**	Sunda Islands.	*Willughbeia firma.* *Leuconotis eugenifolius.* *Parameria glandulifera.*	Balls, sausages, and slabs, in colour similar to Assam.	15–30	7·6	1·3	Good dry lots, highly valued; wet and sticky ones very inferior.
4. **Java and Padang.**	Java. Sumatra.	*Ficus elastica.* *Parameria glandulifera.*	Large red, often translucent pieces.	12–30	5·6	0·8	Dry lots much valued.

5. Borneo.	Borneo.	*Leuconotis eugenifolius.* *Willughbeia firma.*	Large lumps, dark grey outside, white inside.	35–50	2·2	2·2	Clean lots much valued.
6. Ceylon.	Ceylon.	*Manihot glaziowii.*	Irregular tubes. Colour, black and grey.	20	3·2	0·7	Good strong rubber.
7. New Guinea Balls.	New Caledonia.	*Ficus Rigo.*	Strings of small balls, black outside, white or pink inside.	15	4·2	1·3	Unmixed lots very good quality.
8. Dead Borneo. Pontianac.	West Borneo.	?	Greyish-white balls or slabs.	15	85–95	1·8	Very resinous, value very low.
9. Cochin China.	Cochin China.	*Parameria glandulifera.*	Irregular dark brown lumps.	20	6·4	0·5	Very fair quality.

CHAPTER III.

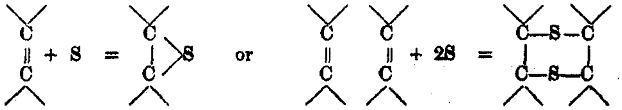
EXAMINATION OF INDIA RUBBER SUBSTITUTES.

(A.) Reclaimed or Recovered India Rubber.

Of late years the use of reclaimed or recovered india rubber, and, as a natural consequence, the manufacture of this article, has assumed very large proportions indeed. The raw material is always either factory scraps and cuttings, or old and worn-out rubber articles of every description.

Generally speaking, the recovery consists in such a treatment as to restore to the india rubber contained in those scraps and old articles its original plasticity and solubility in the technically used solvents, together with its capability of vulcanisation. It is generally considered that the last named requirement is the most difficult to attain, the current idea evidently being that this desirable result has the more or less complete devulcanisation of the waste rubber as its necessary condition. But it is easily shown that the capability of recovered india rubber to vulcanise is necessarily consequent upon the restoration of plasticity in the vulcanised india rubber. As we have seen in the discussion of the vulcanisation problem, the amount of sulphur entering into actual combination with india rubber is not limited to the small proportion of combined sulphur found in ordinary india rubber articles, a proportion rarely exceeding 3 per cent. Vulcanised india rubber, as far as the process of vulcanisation can be chemically interpreted at the present time, is an addition product of the unsaturated polyprene molecule and sulphur. But this addition product is still a highly unsaturated body—so much so, that out of thirty individual ethylene bonds in vulcanised india rubber, on an average, and under ordinary circumstances, not more than two can have become saturated by sulphur addition.[1] This holds true,

[1] This calculation is based on the consideration that, according to Gladstone and Hibbert, india rubber for each $C_{10}H_{16}$ complex contains three ethylene bonds, and further, that the process of sulphur addition to the india rubber must take the form of either



In the first case, for the formation of a vulcanisation product containing about 2·5 per

whatever may eventually be found to be the size of the india rubber molecule.

Now, it is well known that vulcanisation products, with any amount of combined sulphur up to, and most probably exceeding, 20 per cent., may be produced under suitable conditions; and, from the composition of the addition products polyprene forms with bromine or with sulphur monochloride, we may infer that at least twenty out of the thirty ethylene bonds occurring in any given complex of india rubber molecules can simultaneously enter into the process of forming an addition product. Consequently there is no theoretical objection to a true 'revulcanisation' of vulcanised india rubber if we succeed in removing the physical effects of the original vulcanisation—in other words, if we restore to the vulcanised india rubber the plasticity which characterises it in its primitive condition. In the process of revulcanisation, some of those ethylene bonds which remained intact in the first vulcanisation then come into play and take up the sulphur present. This process of recovery and revulcanisation can, moreover, be repeated as long as the recovered india rubber contains any free ethylene bonds, although there is no doubt that the quality of the india rubber deteriorates rapidly with each successive revulcanisation. This is only what is to be expected, considering that with each successive vulcanisation we obtain a product, the composition and constitution of which exhibits an increasing difference from the composition and constitution of the primary vulcanisation product. For whereas the latter is a very highly unsaturated body, with, at the outside, 3 per cent. of sulphur, each successive revulcanisation increases the constitutional saturation, and likewise the percentage of combined sulphur in the product. This, in my opinion, sufficiently explains the fact of the already alluded to deterioration of the product with each revulcanisation—a fact which is certainly no more surprising than the extraordinary change of properties following upon the successive saturation of radicals in the benzene ring.

In the above it is, of course, taken for granted that the sulphur of vulcanisation, the combined sulphur, is not removed in the process of recovery. I am well aware that this assumption is not shared by the manufacturers, who expressly declare their recovered india rubber to be 'devulcanised' or 'desulphurised.' This declaration is, no doubt, made on the strength of the fact that recovered rubber can be revulcanised, the idea being that to produce this result is only possible by removing the chemical cause of the first vulcanisation. Analysis of any sample of recovered india rubber will, however, at once show this conclusion to be erroneous, as in no case is the combined sulphur found to have been eliminated, although most processes, patented or otherwise, for the recovery of india rubber aim at this result. It will, indeed, be generally found that the apparently most

cent. of S, $10C_{10}H_{16}$ containing thirty ethylene bonds would combine with 1S; in the second case, $20C_{10}H_{16}$ with 2S.

promising of these processes are just those that fail most conspicuously to yield a satisfactory product. The most satisfactory processes are invariably those in which no account is taken, chemically, of the combined sulphur, but where such means and agencies are employed as have been found to result merely in the restoration of the original plasticity of the india rubber.

Analysis of a number of representative commercial brands of recovered india rubber, and some others that I prepared myself, gave the following figures :—

	I.	II.	III.	IV.	V.	VI.
Moisture,	·50	·81	·32	...	·14	...
Oils and resins,	10·23	10·62	9·85	18·53	19·44	19·04
Fe_2O_3 and Al_2O_3,	·77	1·01	·88	·79	·38	·19
PbO,	14·20	...	15·30	...	...	...
$PbSO_4$,	3·29	18·88	10·81	...	...	...
ZnO,	...	...	...	...	23·89	21·03
$CaCO_3$,	10·41	...	...	...	...	...
$CaSO_4$,	21·93	26·20	22·77	...	...	...
$BaSO_4$,	...	...	...	...	...	20·85
Carbon,	7·54	8·27	8·49	...	...	...
S free,	·88	·62	·61	·20	·15	trace
S combined,	3·92	2·46	2·71	4·84	4·16	2·28
I. R. substitute,	...	...	...	...	...	9·26
India rubber,	26·32	31·12	28·25	75·63	50·83	27·34
Price per lb.,	5½d.	11½d.	1/5½d.	...	...	...

These figures, to begin with, show that in the recovered india rubber of commerce the price bears no relation to the quantity of india rubber actually present. It may be, and certainly is, influenced by the quality of the india rubber present, which is a point respecting which we are unable, at any rate at present, to give an account in our analyses. But it is perhaps worth pointing out that in the above commercial samples (I. to III.) the price rises in a ratio which cannot possibly represent the ratios of the values of the original india rubbers contained in the scrap from which respectively these three qualities of recovered india rubber were obtained. Likewise these analyses show that commercial recovered india rubber is loaded with a very considerable amount of mineral matter. Sample III. is considered a very high class article of its kind, but it contains as much mineral matter as sample I., which is sold as a low quality. As to the advantage to the manufacturer of this commercial recovered india rubber, a simple calculation of the price of 1 lb. of india rubber in those samples will be found highly instructive.

From the chemical point of view, the respective figures for free sulphur, combined sulphur, and india rubber first attract attention, especially if we calculate in every case the percentage of the two first named items in relation to the india rubber. We then obtain :—

	I.	II.	III.	IV.	V.	VI.
S free,	3·34	1·99	2·15	·26	·29	...
S combined,	14·89	7·90	9·59	6·38	8·17	8·33
India rubber,	100·00	100·00	100·00	100·00	100·00	100·00

What strikes one very forcibly in these figures is the enormous proportion of sulphur of vulcanisation which in every case far exceeds the proportion ever occurring in any commercial vulcanised india rubber manufactured from india rubber in its native state. The first three samples of commercial recovered india rubber are particularly remarkable in this respect, as, to begin with, the total sulphur (free + combined) they contain is, in the case of I., about double the usual amount, and, even in the case of II. and III., either close to or distinctly above the highest limit, which is about 10 per cent. The samples IV. to VI. show an amount of total sulphur which is well within the practically adopted limit, but, nevertheless, even in these three samples the amount of combined sulphur is extraordinarily high, showing percentages which in ordinary vulcanisation are never obtained, and perhaps even not obtainable.

For the elucidation of this surprising fact, as far as the samples I. to III. are concerned, we have no available data. As regards the samples IV. to VI., these were 'recovered' from vulcanised india rubber (Pará), which before recovery showed, on analysis, the following ratios between sulphur and india rubber:—

	IV.	V.	VI.
S free,	4·88	6·49	6·42
S combined,	2·12	2·30	2·47
India rubber,	100·00	100·00	100·00

To begin with, we see from these figures that in the recovery process the percentage of total sulphur is decreased, partly, as will be shown later on, through some of the sulphur volatilising as such, partly through the evolution of sulphuretted hydrogen. But still more important is the fact that these figures show very clearly that the bulk of the free sulphur present enters into combination with the india rubber, so that the recovery process not only effects no devulcanisation, but actually results in a higher degree of vulcanisation of the already vulcanised india rubber. This at once shows conclusively that the efficiency of the recovery process depends entirely upon the solvent or softening actions of the oils or hydrocarbons, which, as far as my experience goes, are at present invariably employed in all india rubber recovery processes. It is also obvious that the great inferiority of even the best recovered india rubber to the native article is due to this further vulcanisation during the process of recovery.

It would be exceedingly interesting to examine the effect of this recovery upon an india rubber article largely or entirely composed of once recovered india rubber. It is almost certain that such successive recoveries will result in a progressive increase of the combined sulphur of vulcanisation, and a consequent rapid deterioration in value of the recovered product; and I suggest that this theory might be found to account for the enormous percentages of combined sulphur in the above samples I. to III. Whether such successive recoveries, independent of the quality of the recovered product, can be effected a number of times, leading eventually to a saturated polyprene polysulphide, or whether there is a limit to this number, and by what that limit is determined, cannot at present, in the absence of all experimental data, be decided. There can be, however, no doubt that the recovery processes at present conducted must, after a few repetitions, yield products no longer suitable for manufacturing purposes.

Information as to the actual recovery processes employed is very scarce, the methods employed being kept jealously secret. From this it should not be inferred that these processes are of any particular merit—indeed, the analysis of any sample of commercial recovered india rubber amply proves them to be of a highly primitive and empirical description. The fact that every sample of recovered india rubber contains from 8 per cent. upwards of mineral oils, sometimes even fatty oils, or a mixture of the two, shows that the recovery process, generally speaking, consists in treating the vulcanised india rubber with oil under certain conditions. The oils I have so far found in samples of recovered india rubber are either ordinary mineral oils, such as vaseline oil, petroleum jelly, or rosin oil; or vegetable and fatty oils, such as castor oil or colza oil. Experiment shows that the action of any of these oils upon vulcanised india rubber at ordinary temperatures is extremely slow, but quickens as the temperature rises. The best results appear to be obtained at temperatures lying below the upper limit of the range of temperatures at which vulcanisation is carried out. The heat may be applied to the mixture of vulcanised india rubber and oil, either externally, or by treating the mixture in closed vessels with superheated steam at the requisite temperature, or the two modes of heating may be combined. The latter is most probably the way by which the best results are obtained.

This recovery process can scarcely be expected to effect devulcanisation of the vulcanised india rubber, and, indeed, as I have shown above, it actually does just the reverse. Of processes devised to accomplish devulcanisation, as distinguished from mere recovery as above outlined, only two or three have been proposed. The first is due to A. F. B. Gorness (Germ. Pat., 62,738/1892), and consists in the treatment of the vulcanised substance first with iron filings and dilute sulphuric acid, followed by treatment with some alkaline solution. The less said about this process the better. Another process proposed by Michelin & Co. (Germ. Pat., 75,063/1894) looks more rational. It is based upon the well-

known affinity of finely subdivided metals, such as copper, tin, lead, mercury, and others, for sulphur. It is proposed to mix these metals intimately with the india rubber to be devulcanised, then to treat this mixture with an indifferent india rubber solvent, such as benzene, toluene, chloroform, or carbon bisulphide. It is stated that under these conditions devulcanisation takes place, the regenerated india rubber passing into solution. Very similar to this is GERBER'S Patent (Eng. Pat., 19,284/1893), according to which the vulcanised india rubber, containing from 5 to 8 per cent. of sulphur, is treated, under a pressure of three or four atmospheres, and with constant agitation, with three and a half times its weight of toluene and one fourth its weight of tin, or any other sulphide forming metal. The heating is continued for eight hours, when the resulting solution is poured off and allowed to settle.

It is hardly probable that any of these processes will answer its purpose: certainly not, unless the combined sulphur in vulcanised india rubber proves to be far more active than we know it to be in other organic sulphides—an assumption not warranted by facts.

There is, however, yet another kind of recovered india rubber in the market, mention of which should not be omitted. This is the india rubber recovered from the cuttings of waterproof cloth vulcanised by the cold process (PARKE'S). In this case the aim is to free the cuttings from all textile materials. The remaining india rubber scraps represent only semi-vulcanised india rubber, owing to the cold vulcanising process leaving the deeper layers or coats of india rubber on the cloth almost untouched, and consequently these scraps can again be worked up into coherent masses between hot rollers. This kind of recovered india rubber, of course, still contains the chlorine derived from the sulphur monochloride, and consequently it cannot be used for 'dry heat' mixings, but should again be used for the manufacture of 'cold cured' articles.

A great number of purely empirical processes for the recovery of india rubber—that is, processes not based upon a well-understood chemical reaction—have been suggested and patented. None of them solves the question of devulcanising the india rubber. At most, an attempt has been made to remove the free sulphur by boiling the ground scraps with aqueous solutions of alkalies or alkaline carbonates. It is scarcely doubtful that, with a view to ultimate devulcanisation, the removal of the free sulphur is of great importance, and this is also easily and cheaply accomplishable; but the attempt to effect final devulcanisation by treatment of this partly desulphurised india rubber with ordinary rubber solvents is certainly inadequate. What is evidently required is a treatment with reducing agents, and from that point of view some of the above quoted patents, employing metals in the molecular state, appear rational. Experiments I made in this direction gave, however, most discouraging results. Nevertheless, further research on these lines should be made. It must be borne in mind that the conditions of these reduction experiments,

in which, as long as metallic powders are employed as reducing agents, both the reducing agent and the body to be reduced are present and remain throughout the process in the solid state, are not very conducive to success. The vulcanised india rubber being unavoidably solid, the reducing agent should certainly be liquid, or, if a solid, it should be used in solution. If this is so, the use of metallic reducing agents will have to be abandoned, and liquid or soluble reducers should be tried instead.

The analysis of recovered india rubber is, of course, carried out on exactly the same lines as that of ordinary india rubber articles. The various points to be determined are:—

1. Specific gravity.
2. Acetone extract.
3. Nitrobenzene (nitro-naphthalene) extracts.
4. India rubber substitutes (fatty)—{ S in substitute. / Cl in ,, }
5. India rubber—combined S.
6. Carbonaceous matter.
7. Mineral constituents.

The working details of these analyses will be found in a later chapter.

A few words are, however, necessary concerning the interpretation of the analytical results, for the simple reason that data which would be considered satisfactory in an ordinary india rubber article would at once condemn a sample of recovered rubber, and *vice versâ*.

1. **Specific Gravity Determination.**—This is carried out in the usual manner by means of the pyknometer. The test is of comparatively little importance.

2. **Acetone Extract.**—The ratio between the percentage of acetone extract and that of india rubber present in the sample is of considerable moment in judging the intrinsic quality of a sample of recovered india rubber. It may safely be assumed that the higher this ratio, the poorer is the quality of the recovered india rubber. The amount of acetone extract is indeed a reliable index of the efficiency of the process, whichever it be, by which the recovery has been effected, especially if we calculate the percentage of acetone extract upon the actual amount of india rubber present. In doing this, it will be found that the vast majority of commercial brands of recovered india rubber rarely yield less than 20 per cent. of extract. The extracted residue will then frequently be found to consist of a dry, crumbly mass, possessing very little elasticity and still less plasticity. The value of such a recovered india rubber is scarcely higher than that of a mixture of ground rubber scraps (vulcanised), with a corresponding proportion of oil. In a good recovered india rubber the percentage of oils or hydrocarbons should be below 10 per cent. (the lower the better), and the residue after the extraction should itself possess an appreciable amount of plasticity. When this is not the case, the manufacturing value of the recovered sample is really only that of a mere 'filling'—*i.e.*, bulk-giving substitute.

In many cases it may also be advisable to examine the nature of the acetone extract specifically, by estimating the amount of saponifiable matter it contains by KOETTSTORFER'S process. The saponification number of the extract should be very low, as the presence of an appreciable quantity of fatty oil in recovered india rubber is apt to cause serious trouble. It becomes, therefore, rarely necessary to attempt the identification of any fatty oil present, but it is generally desirable to convert the observed saponification number into a figure expressing the percentage of fatty oil in the extract. The kind of fatty oil present being generally unknown, the simplest way towards an approximation is to ascribe to the fatty oil a mean saponification number of 190. The percentage of fatty oil in the extract may then be calculated by means of the formula,

$$\% = \frac{100\, n}{190\, w}$$

in which n is the number of milligrammes of potassium hydroxide that disappeared in the saponification process, and w the weight of the acetone extract used for saponification.

3. **Nitrobenzene Extract (cold).**—This process, suggested by HENRIQUES (*see* page 242) for the detection of asphaltum in india rubber articles, may be employed for the same purpose in the analysis of recovered india rubber. The process, is, however, scarcely a very satisfactory one, as, on the one hand, not every specimen of asphaltum is readily or completely soluble in slightly warm nitrobenzene, and, on the other hand, coal tar and coal tar preparations, which are freely employed in the production of a number of india rubber manufactures, will also dissolve to greater or less extent in the same solvent. Its usefulness is, however, unquestionable, as it permits of the removal of certain organic non-rubber components, which could not be eliminated either by the acetone extraction or by the later treatment with alcoholic caustic soda.

4. **India Rubber Substitutes** (fatty).—The detection and estimation of these very largely used so-called substitutes is based upon the saponifying action of alcoholic caustic soda upon them. This valuable process, which is also due to HENRIQUES, is fully described in a later portion of this book. To obtain the correct figure of the sulphur of vulcanisation contained in the india rubber of a sample of recovered rubber, the determination of the sulphur in the soda extract is indispensable. The test for chlorine and its determination in this extract should likewise never be omitted.

5. **India Rubber and Combined Sulphur.**—The sample which has served for the three last named tests is carefully dried under conditions preventing its oxidation, and accurately weighed out into two exactly equal portions—one of which serves for the estimation of the india rubber, the other for the determination of the combined sulphur. The processes adopted are, of course, exactly the same as those used in the analysis of ordinary india rubber articles.

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6. **Carbonaceous Matter, and 7. Mineral Constituents.**—The insoluble residue remaining after the resolution of the india rubber by means of boiling nitrobenzene retains all the mineral and carbonaceous matter contained in the original sample. It may also contain vegetable and animal fibres. The separate estimation of these in the presence of carbonaceous matter is scarcely feasible, but their presence should be noted as objectionable. The determination of the carbon, or carbonaceous matter, in cases where an absolutely correct analysis is required, is rather troublesome. It is carried out as described in Chap. IX. (page 252). Where no carbonaceous matter is present, the usual lines of inorganic analysis are followed.

The most important criteria as to the quality of a sample of recovered rubber are the amounts of india rubber, free sulphur, and sulphur of vulcanisation present. As regards free sulphur, I consider its presence in any appreciable amount as a sure indication that not even an attempt at devulcanisation, the only satisfactory aim of recovery, has been made. Any treatment calculated to eliminate the sulphur of vulcanisation would be certain to effect, in the first instance, the removal of some of the free sulphur. No doubt it is quite possible to remove the free sulphur without producing devulcanisation, so that the absence of sulphur in this form could not be held to prove that even a partial actual devulcanisation has been effected; but I have satisfied myself by numerous experiments that all known processes for the production of recovered rubber, when carried out in the presence of free sulphur, invariably affect the result detrimentally, so that, as I stated above, the presence of free sulphur may safely be taken to prove the employment of an irrational recovery process.

All recovering processes at present in use, as far as is known, are carried out at temperatures above 150° C. At this temperature free sulphur contained in the india rubber under operation may partly sublime, or enter into combination with metallic oxides contained in the india rubber, or interact with the oils or other substances employed in the process. It is therefore even possible for a sample of recovered rubber to have passed through the recovery process with all the free sulphur in it, and in the end to be altogether free from this element. Whether this can be accomplished in this manner without injury to the rubber it is impossible to say: as far as my experiments go, they show that this result can only be obtained at an inordinately high temperature. Such a sample may then contain no free sulphur and still be objectionable, as in this case freedom from sulphur has been purchased at the expense of the india rubber, which at the high temperature at which recovery was effected underwent partial decomposition. It is therefore important, for the purposes both of practical assay and of experimental research on the question of recovery, to possess means to enable us to detect the presence of decomposition products of india rubber in the recovered article.

Now, the fact that such decomposition products, if present, were formed in the recovering process, not so much through chemical action as through

the action of heat, at once suggests that we may expect them to be substances of the kind we encounter amongst the products of the dry distillation of india rubber, or, what is even more likely, similar to those obtained in boiling india rubber in nitrobenzene. But in either case we may expect them to be soluble in acetone—in other words, they will form part of the acetone extract, the importance of ascertaining which we have already discussed. The detection and estimation of these decomposition products in the presence of the oils, resins, and paraffin wax almost invariably occurring in recovered india rubber is, however, no easy matter. A separation of these substances from the decomposition products of the india rubber by solvents appears to be impossible. Fairly satisfactory results may, however, be obtained by utilising the fact that the decomposition products of india rubber are terpenoid bodies,[1] which form bromine addition products containing upwards of 60 per cent. of bromine. These are insoluble in alcohol, and very difficultly soluble in benzene; whereas any bromine addition or substitution products of the oils occurring in recovered india rubber are readily soluble in both alcohol and benzene, and also in a mixture of the two. Therefore, if we dissolve the acetone extract, after distilling off the acetone, in just sufficient of a mixture of two volumes of benzene with one volume of absolute alcohol to dissolve the whole of the extract, and then add bromine to slight excess, we obtain, if decomposition products of india rubber are present, a precipitate consisting of the bromine addition products of the latter. This can be filtered off, and should be washed first with the mixture of benzene and alcohol, and finally with absolute alcohol. It is then dried at a temperature not exceeding 50° C. The composition of this bromo-derivative, although constant for the same sample of vulcanised india rubber or its decomposition products, is not so for different samples of vulcanised india rubber. The reason for this has been already fully dealt with,[2] but for our present purpose has to be borne in mind. It necessitates an estimation of the bromine in the dried and weighed bromo-derivative, and from the weight of the latter must be deducted the weight of the total bromine contained in it. The result gives us, then, very approximately the quantity of soluble decomposition products of the india rubber of a given sample of recovered rubber. The following figures were obtained in this manner:—

Description of Sample.		5 grms. yield Acetone Extract.		Bromo-Derivative.	Bromine.		Decomposition Product.	
		percent.	grms.	grms.	percent.	grms.	grms.	percent.
American	No. 1 black, .	9·94	·497	·117	66·66	·078	·039	·78
	No. 2 ,, .	9·38	·469	·128	67·10	·086	·042	·84
	No. 3 grey, .	10·11	·505	·151	65·56	·099	·052	1 04
English	No. 1 black, .	12·00	·600	·314	64·96	·204	·110	2·34
	No. 2 ,, .	10·40	·520	·233	65·66	·153	·080	1·60
	No. 3 ,, .	14·27	·713	·581	63·85	·371	·210	4·21
French	No. 1 grey, .	11·67	·583	·661	64·29	·425	·236	4·73
	No. 2 ,, .	10·35	·517	·654	62·53	·409	·245	4·92

[1] *See* page 22 *ff.*

[2] *See* page 11.

All the above percentages are calculated upon the india rubber only contained in each sample, irrespective of anything else present. The above acetone extracts consisted, to much the greater part, of mineral oil. No. 1 of the American samples contained vaseline; the two French samples paraffin wax.

The percentage of 'decomposition product' contained in a sample of recovered rubber is well illustrated by the following analyses of three samples prepared from the same ground rubber scrap with the same amount of mineral oil, but treated at different temperatures.

Sample.	5 grms. yield Acetone Extract.		Bromo-Derivative.	Bromine.		Decomposition Product.	
	p.c.	grms.	grms.	p.c.	grms.	grms.	p.c.
No. 1 treated at 140° C.	10·44	·522	·149	61·74	·92	·057	1·16
No. 2 ,, ,, 160° C.	10·84	·542	·239	61·08	·146	·093	1·86
No. 3 ,, ,, 185° C.	11·62	·581	·325	61·53	·199	·126	2·53

The above figures show that much valuable information is to be gained from the estimation of the decomposition products in recovered india rubber. Of course I do not suggest that this determination should be carried out with every sample of recovered india rubber which is in any way analytically examined. But the fact that such an examination is at all possible is well worth recording, and, moreover, the method is not only useful for the purpose for which we have been discussing it, but will most likely also render useful service in the analysis of decomposed india rubber articles, and investigations into the cause of such decomposition. It is, moreover, noteworthy that the bromine percentages given above fall far short of what is required for the polyprene tetrabromide, and, moreover, exhibit considerable variations in this respect. It is highly probable that the degree of vulcanisation of a sample of india rubber is, to a large extent, if not entirely, responsible for this difference and its variation; and if this should be so, the above method could be modified into a chemical test for the degree of vulcanisation of vulcanised india rubber. On the other hand, the effect of oxidation upon india rubber would likewise tend to reduce its bromine absorption, so that the above method can no doubt also be employed to throw light on this still very obscure subject. Altogether, I think there are enough reasons to make this method one of peculiar interest to the chemist engaged in the analysis of india rubber, and it offers in itself a wide field for promising research in a number of almost unexplored directions.

B. Fatty and other Organic Substitutes.

The number of 'Rubber Substitutes' which have been proposed is legion, and the annual patent registers of all manufacturing countries invariably

record a number of more or less new preparations intended to serve the same purpose, but scarcely any one of which seems even to pass into the advanced experimental stage, and I am not aware that any single one of these preparations suggested during the last ten or fifteen years has found practical employment to any appreciable extent. Indeed, although certain preparations, which we are about to discuss in the following pages, have been for a long time, and still are at the present moment, largely employed under the name of rubber substitutes, it must at once be said that this description as applied to them is a misnomer. We know at the present time of no manufactured product which in any way would deserve the name of rubber substitute. All the substances so described are pure and simply organic adulterants, as distinguished from inorganic or mineral bulking or filling agents. They reduce the quality of an india rubber article exactly in the proportion in which they are present in the article, and the justification of their use lies purely in the popular demand for cheapness.

All the rubber substitutes which at the present time are of any commercial importance are obtained from one or other of the 'unsaturated' fatty oils, either by a process of oxidation, or by treatment at higher temperatures with sulphur, or by treatment with sulphur monochloride in the cold. The process of manufacture of these products will be found below under the various headings descriptive of each of them.

All these so-called 'substitutes' have one and the same fault in common, which lies in the fact that their typical chemical character is still that of a triglyceride. They are, therefore, all readily saponifiable by any of the ordinary means of saponification. In this respect more particularly the action of alkalies and high pressure steam deserves consideration. The latter especially represents a condition to which a very large and important class of india rubber manufactures is continually exposed, and therefore the use of these substitutes in the manufacture of such articles must be strongly condemned. It might perhaps be objected that the saponifying action of high pressure steam is of no practical importance owing to the imperviousness of india rubber, but, in reality, this counts for little. The saponification begins at the surface, but proceeds apace, chiefly owing to the corrosive (dissolving) action of the free fatty acids formed upon the india rubber. As far as the author is aware, the 'moist heat' English Admiralty Test[1] for india rubber goods is the outcome of purely empirical experiments and considerations, but it finds its entire justification and rational explanation in the above noted behaviour of the india rubber substitutes to high pressure steam. The Admiralty test is simply a rough and ready test — what is euphoniously called a practical test—for the presence of 'substitute' in an india rubber article.

In articles which under ordinary conditions of use are exposed neither

[1] *See* page 229.

to the action of alkalies nor to the influence of high pressure steam, the presence of these substitutes is less objectionable, and the justification for their employment in these cases rests upon the price of the articles in question. It should, nevertheless, be pointed out that admixture with substitutes invariably tends to shorten the life of an india rubber article, generally increases its liability to decay, and greatly diminishes its resistance to friction and to torsional or longitudinal stresses.

The above remarks concerning the use of substitutes in india rubber goods apply equally to all the substitutes which are in the market at the present time. It is therefore of considerable importance to examine, in the first instance, the considerations upon which the quality and suitability of an india rubber substitute may be determined with a view to its employment in manufacturing, and also what methods we possess for the detection and quantitative determination of rubber substitutes in rubber articles. But while doing so, a rough outline of the manufacture of the most important substitutes in use at the present time may also be found helpful.

The Manufacture of Rubber Substitutes from Fatty Oils.—The origin of the manufacture of rubber substitutes from fatty oils probably dates back to a much earlier time than the india rubber industry itself. Preparations obtained by heating linseed oil with sulphur were probably known to the alchemists. At any rate, under the description of 'oleum lini sulphuratum,' or 'balsam sulphuris,' they occupied an important place amongst the remedies of our forefathers, and, indeed, are even yet retained in the pharmacopœias of most countries. The fact, that under certain conditions, as regards degree of temperature and time during which the heat was applied, elastic solids are obtained by this process, would soon be observed, and when, towards the middle of this century, the manufacture of india rubber articles became established, the remarkable similarity between india rubber and these sulphuretted oils could not fail to attract attention and suggest the use of such products in conjunction with india rubber. Accordingly, we find that the first rubber substitute which appeared in the market, and which to this day still holds the field, is a product obtained by the interaction of linseed oil and sulphur.

The action of sulphur upon unsaturated fatty oils is by no means completely understood. ALTSCHUL[1] showed that two different compounds are formed according to the temperature at which the reaction takes place. At temperatures not exceeding 150° C., up to 16 per cent. of sulphur are at first dissolved, and after some time absorbed by the oil. At this point it will be found that a drop of the oil, on being brought upon a glass plate, no longer turns milky or opalescent, owing to merely dissolved sulphur crystallising out, nor does precipitation of sulphur occur on dissolving the oil in ether. As, moreover, this point can be reached without any appreciable quantities of hydrogen sulphide being evolved, we may

[1] *Zeitschr. f. angew. Chem.*, 1895, p. 535.

infer that this absorption of the sulphur by the oil under the above stated conditions is an addition process pure and simple.

If the interaction between the unsaturated oil and sulphur is carried on at temperatures from 150° C. upwards, the evolution of hydrogen sulphide becomes more marked as the temperature increases. This is accompanied by a very considerable thickening of the oil, which eventually becomes perfectly solid. Substances solidified in this manner are prepared at present from a great variety of oils, such as linseed, colza, castor, cotton seed, and maize oils, and these products are largely used as so-called rubber substitutes, although in reality they are nothing but organic filling or bulking material.

In preparing such substitutes, the quantity of sulphur employed is, of course, a matter of some importance. Nevertheless will it be found that the commercial products vary very greatly in this respect, the percentage of sulphur in them being often as low as 5 per cent., and, on the other hand, exceeding in many cases 17 per cent. This is, in the first instance, due to the fact that, instead of employing for the manufacture of these substitutes the above named oils in their natural state, 'blown' oils are used—*i.e.*, oils which have been treated with air or oxygen at higher temperatures. In this treatment oxygen addition products are formed, the oxygen combining with the unsaturated fatty acid of the glyceride. This is accompanied by a thickening of the oil, which becomes more pronounced the greater the amount of oxygen taken up by the oil, although there is no doubt that this treatment, at the temperature at which it is effected, leads to further effects which tend to increase the viscosity of these oils. The treatment may be carried so far, that eventually the oil is converted into a more or less 'dry' and resilient solid (*see* below); but for the purpose of the manufacture of the sulphuretted substitutes, the 'blowing' is only carried far enough to reach a specific gravity of about 0·960. The constitution of the addition products thus formed is entirely conjectural, but the effect of this oxygen addition is, of course, a reduction of the state of non-saturation of the oil, and consequently a smaller percentage of sulphur is necessary to convert one of these 'blown' oils into a completely saturated compound than would be required for the natural oil. In the trade the substitutes made from blown oils are described as 'floating substitutes' owing to their property to float on water, which, of course, is due to their specific gravity being slightly less than that of water; while the substitutes made from ordinary oils possess a specific gravity higher than that of water, and so are non-floating.

There are two points as regards substitutes of the above description upon the careful control of which depend their satisfactory working in the factory, as well as the life of the articles manufactured with their aid. These two points are (*a*) the amount of soluble fatty oil they contain, and (*b*) the amount of free sulphur. Both these quantities should be as low as possible. A high percentage of soluble fatty matter invariably shortens the life of

the india rubber, and a high percentage of free sulphur would either require a diminution in the proportion of the substitute used, or, if unnoticed, might lead to serious mishaps in the vulcanisation process. This is an obvious point, which, however, is often neglected, not infrequently with disastrous results. In calculating the amount of sulphur to be added to a rubber mixing containing substitute, the amount of sulphur present in the latter should evidently be deducted, and for this reason it is most important that this amount should be accurately known.

Some typical samples of brown substitute gave the following results on analysis :—

	I. French Make.	II. English Make.	III. American Make.
Free S,	2·31 p.c.	2·41 p.c.	5·22 p.c.
Combined S,	6·58 ,,	6·84 ,,	19·81 ,,
Soluble oil,	2·20 ,,	2·40 ,,	9·78 ,,

Samples I. and II. are practically identical. Sample III. I consider a rather objectionable specimen, not so much on account of its rather high percentage of free sulphur, as on account of the large proportion of soluble oil it contains. This sample has been made from maize oil.

Now it might appear that samples I. and II., which are curiously similar in composition, would also in their working produce the same result. This, however, these analytical data do not enable us to infer. Indeed, there is no analytical method which would allow us to decide upon the quality of two different brands of brown substitute which are, like the above, practically similar in their chemical constants. Nevertheless, we are able to decide this question by examining mixtures of india rubber and these substitutes microscopically. Mixtures of these two substances, of course, do not represent intermolecular penetration of the constituents as do true solutions, but are a sort of solid emulsions of the substitute in the india rubber; and we may therefore judge the quality of two substitutes by determining which of them forms the finest emulsion. The difference in this respect is often very great even in samples which are apparently chemically identical. In bad cases no granular emulsion is obtained at all, but the substitute breaks up into a mass of streaky or scaly flakes. Practical experience has shown this microscopical test to be invariably reliable and trustworthy. Details regarding the working of this test will be found in the analytical portion of this chapter.

There is, however, another class of substitutes which is distinguished from the 'brown substitutes' above described by the name of white substitutes, and which is formed by substances produced by the interaction of sulphur monochloride and unsaturated oils. ULZER and HORN,[1] who were the first to investigate the products of this reaction, found them to

[1] *Jahresber. d. chem. Technol.*, 1890, p. 1177.

consist of glycerides, the fatty acids of which contain chlorine and sulphur. They further found that these products can be saponified with alcoholic caustic soda, during which process all the chlorine is eliminated from the fatty acid, which, however, retains its sulphur intact. HENRIQUES[1] has very considerably extended ULZER and HORN's work, and established the fact that these white substitutes are simply addition products of the fatty oils and chloride of sulphur. In accordance with this fact, we find that the iodine absorption of these substitutes is very much smaller than that of the oils from which they were produced.

The simplest way to produce these substitutes is by mixing the fatty oil with a certain quantity of chloride of sulphur and agitating the mixture well. In a very short time a vigorous reaction sets in, the mixture getting very hot, evolving vapours of sulphur monochloride, and also small quantities of hydrochloric and sulphurous acid. Simultaneously the mass thickens, and is rapidly converted into a solid, semi-transparent, elastic substance, the colour of which varies from a pale amber colour to a more or less pronounced brown. This product generally feels the 'dryer,' the darker its colour. It is easily ground into a mass of fine flakes of much lighter colour than the original substance. As is to be expected, the result depends very much upon the proportions of oil and sulphur monochloride employed, and also upon the kind of oil used. HENRIQUES[2] determined the proportion of sulphur monochloride required to produce dry solid substitutes with various kinds of oils, and obtained the following figures:—

100 parts	of linseed oil	require	30	parts	of S_2Cl_2.
,,	,, poppy seed oil	,,	35	,,	,,
,,	,, colza oil	,,	25	,,	,,
,,	,, cotton seed oil	,,	45	,,	,,
,,	,, olive oil	,,	25	,,	,,
,,	,, castor oil	,,	20	,,	,,

It must, however, not be assumed that the products obtained from these oils by their interaction with sulphur monochloride form all equally satisfactory 'rubber substitutes.' This is, indeed, not the case. Especially the product obtained with castor oil has been found wanting in stability, but also the substitutes from olive oil and linseed oil proved defective in this respect. At the present time a well-refined German seed, colza oil, is used for this purpose, to the exclusion practically of any other oil. HENRIQUES[3] patented the use of oxidised (blown) oils for the manufacture of these substitutes, and he claims that in this manner he obtains substitutes which are not only cheaper than substitutes prepared from natural oils, owing to the considerably smaller quantities of sulphur monochloride required for their conversion, but he also states them to be superior to the ordinary substitutes. The latter claim is certainly not in accordance with the experience obtained with such substitutes in English factories, where

[1] *Chem. Zeitg.*, 1893, p. 707. [2] *Ibid.*
[3] Germ. Pat., No. 73,045, 1893.

they were tried fairly and extensively years before the date of HENRIQUES' patent.

In preparing these substitutes on the large scale, the most important point is to control the reaction so as to prevent a rise of temperature of above 70° C. in any part. For this reason it is generally recommended to prepare them in small quantities at a time. SCHULZE[1] states that not more than 20 lbs. of oil should be treated at a time. As a matter of fact, much better results are obtained by working with 3 to 5 cwt. batches, but in order to check the reaction, the addition of a suitable quantity of some hydrocarbon, the boiling point of which should not exceed 70° C., is necessary. Also SCHULZE'S statement, that the operation should not be carried out in wooden vessels, is without justification. Of course, when preparing these substitutes on such a large scale, open vessels can no longer be employed, and a closed apparatus with an effective vapour-condensing plant attached must be used.

The relative nature of both the 'brown' and 'white' class of substitutes above described is very clearly brought out by the analytical results published by HENRIQUES,[2] and given on the following page.

It is obvious from these figures that there can hardly ever arise any doubt as to whether a fatty substitute contained in an india rubber article is a brown or a white substitute. The readiness with which these substitutes are saponified by alcoholic caustic soda renders their complete extraction from the finely ground india rubber sample an easy matter. The amount of substitute present in any given sample cannot, of course, be estimated by direct methods—at any rate, in most cases without liability of considerable error. It is therefore estimated by the loss in weight of the sample after treatment with alcoholic caustic soda. The amount of chlorine extracted by the alcoholic caustic soda decides, of course, the nature of the substitute present.

The general practice is to use the brown substitutes for 'dry heat cured' goods only—*i.e.*, goods vulcanised with sulphur; and the white substitutes for 'cold cure' goods—*i.e.*, goods vulcanised with chloride of sulphur (S_2Cl_2). There is, however, a certain class of 'dry heat cured' goods, for the manufacture of which white substitute is employed. This at first sight appears surprising, in view of the fact that white substitute already at a temperature of 90° C. loses a considerable part of its chlorine in the shape of hydrochloric acid; and at vulcanising temperature—130° C. —this effect of heat upon white substitute becomes considerably more noticeable. It might, therefore, be thought that on hot vulcanising a mixing containing white substitute, a considerable risk of 'blowing' was incurred owing to the evolution of hydrochloric acid gas by the substitute; but in practice, provided the mixture does not contain any inorganic carbonates or sulphides which are acted upon by sulphuretted hydrogen, the curing of such a mixture causes no difficulty whatever, and

[1] *Gummi Zeitung.*, 1898, p. 811. [2] *Chem. Zeitg.*, 1893, p. 707.

Analytical Tables.

	Commercial Products.					Linseed Oil Substitutes.		Colza Oil Substitutes.		Substitute from Oxidised Poppy-seed Oil.	Substitute from Oxidised Lin-seed Oil.	Castor Oil with minimum S_2Cl_2.	Substitutes with maximum S_2Cl_2	Substitute from Oxidised Cotton Oil.
	White Substitute.			Brown Substitute.		Prepared from Natural Oil.	Prepared from Oxidised Oil.	Prepared from Natural Oil.	Prepared from Oxidised Oil.					
	A.	B.	C.	A.	B.									
Sulphur in substitute,	6·4	6·17	8·25	15·48	17·71	9·34	4·78	8·28	6·59	7·68	...	4·82	10·6	6·23
Chlorine ,, ,,	5·0	5·86	8·88	0·7	0·36	8·84	4·85	7·62	5·95	7·44	...	6·70	8·95	5·36
Water ,, ,,	0·85	1·0	...	...	...	3·02	0·85	...	...	...	...	...	...	...
Ash ,, ,,	0·8	5·51	...	...	...	...	...	...	...	...	...	...	...	...
Fatty acids,	90·45	73·58	...	...	...	79·6	87·67	86·89	87·95	74·90	...	85·35	...	...
Sulphur in fatty acids,	6·12	6·45	8·15	14·14	15·20	9·88	4·06	8·34	6·54	8·32	...	5·32	...	6·44
Chlorine ,, ,,	0·83	0·43	...	...	...	little	0·60	little	little	...	...	0·26	little	little
Iodine number of substitute,	30·9	31·0	32·6	42·0	42·0	56·3	52·6	32·5	26·9	33·6	42·8	35·2	21·9	30·3
Iodine number of fatty acids,	91·3	91·2	102·3	129·0	125·6	160·3	{ 141·2 } { 121·0 }	101·5	102·8	133·3	129·2	147·4	143·5	91·5
Acetyl number,	...	...	...	...	...	21	19·6	31	...	...	...	...	105·6	51·3

there is certainly no escape of hydrochloric acid noticeable. This apparent anomaly, no doubt, finds its explanation in the existence of a polyprene dihydrochloride, in the fact that india rubber forms an addition product with hydrochloric acid. Although this addition product under the influence of heat gives off hydrochloric acid, this process (*see* page 146) is very far from complete; and as the white substitute at vulcanising temperature also parts with a certain fraction only of its chlorine in the form of hydrochloric acid, it follows that under practical conditions the amount of hydrochloric acid evolved by the substitute always falls considerably short of the quantity india rubber can absorb and retain at vulcanising temperature. This is all the more so, as the quantity of white substitute which can be used in admixture with india rubber for the manufacture of 'dry heat' goods is limited by the fact that such mixtures, in order to ensure satisfactory vulcanisation of the india rubber, require quantities of sulphur increasing rapidly with the proportion of substitute present, so that, for the vulcanisation of mixtures in which white substitute predominates, quite enormous proportions of sulphur (over 30 per cent.) would be required. It cannot be said that goods of this description are not made, but that they should be must be regretted, the more so as the only reason for the employment of white substitute in 'dry heat' goods is the colour of the finished substance. Brown substitute, of course, produces goods of a somewhat dark-yellowish or brownish-grey colour, but the trade insists upon having certain articles, gas-tubing especially, of a light greyish-white colour, which can only be obtained by means of white substitute. There is nothing, apart from the question of colour, to commend the use of white substitute in 'dry heat' goods—indeed, the practice is unquestionably detrimental to the quality of these goods.

The above described 'brown' and 'white' substitute represent probably fully 90 per cent. of all the so-called rubber substitutes used. How little they really deserve this name has already been shown in the introduction to this chapter. Nevertheless, every year unfailingly produces its regular crop of 'inventions,' which in their early stages are generally stated to realise the production of artificial india rubber, but which are simply the application of the above described reaction of sulphur, or chloride of sulphur, upon fatty oils, upon either some new kind of oil, or upon an oil subjected to some preliminary treatment (blowing), or upon such oils under conditions more or less novel—generally less. Of all these new substitutes there is only one which has been at all able to obtain some foothold in the market, though it could by no means be said to be firmly established at the present. This is the curious product named, after its inventor, *Fenton rubber*. This substitute is manufactured[1] by mixing oxidisable vegetable oils, either in the raw or oxidised state, with certain proportions of tar, pitch, creosote, or 'other form of pyroligneous acid,' and placing "the mixture, either cold or previously heated together, into a bath of diluted

[1] Eng. Pat., No. 26,548, 1896.

nitric acid, and allowing it to remain for maceration—cold, or quickening the action by boiling—until the whole is coagulated into a tough elastic magma 'having the appearance' and nature of caoutchouc-like substance." This product is poured upon pans and roasted for a short time, "when it coagulates into a highly elastic mass in appearance like india rubber, and can be vulcanised exactly as that substance is."

This is simply a re-invention of a process first employed in 1848 by SACHS and JONAS, with the very questionable 'improvement' of the addition of tar, pitch, creosote, or 'other form' of pyroligneous acid.

The rubber substitutes we have been considering so far are all intended to replace part of the india rubber in rubber mixtures. There is, however, a very numerous class of substances which are actually intended to replace india rubber entirely for both soft and hard rubber (ebonite) articles. Attempts in this direction up to now have always failed, and probably always will, if these substitutes are used for articles in which high tensile strength, great elasticity, resistance against abrasive forces, and indifference to chemical, especially alkaline, reagents, are chiefly required. Where waterproof qualities, electrical insulation resistance, sound-deadening, and similar qualities only are required, such substitutes may be more or less serviceable. In the past they have been greatly discredited, owing to the immoderate claims put forward on their behalf—claims which it was invariably found could not be sustained.

The number of patents which have been taken out for rubber substitutes of this description is truly appalling, and becomes still more so when we discover that, with only an occasional exception, all these patents are based upon two reactions: either the action of sulphur upon fatty oils, or the action of oxygen upon oxidisable oils. And herein lies the weak point of all these substitutes: they are all saponifiable, and they all lack the resistance possessed by india rubber to temperature changes within comparatively wide limits. To call these substances india rubber substitutes, or artificial india rubber, is grossly misleading. They can in no case compete with india rubber, and their use begins only where that of india rubber ceases—*i.e.*, uses where such highly compounded (mineralised) mixings are required, that the india rubber acts more or less exclusively as a cement for the mineralic powders only, as is the case in the very lowest classes of india rubber goods.

It is impossible to give even an outline of all the patents that have been taken for the manufacture of such substitutes, nor would such an outline be at all worth the trouble. Even the latest patents in this direction represent no progress over the methods which were employed for the same purpose thirty years ago. What little actual improvement there is, is simply one of manipulation. We may therefore confine ourselves to a brief exposition of the mode of manufacture of one of the more recent of these compounds, known as 'Oxolin.'

This is one of the innumerable patents based upon the formation of

solid products by the oxidation of linseed oil. In this case this is performed by impregnating vegetable fibre, such as flax, hemp, or jute, with linseed oil in a hydro-extractor. The impregnated material is then spread on trays and oxidised by exposure to the air at a temperature of about 45° C. This operation is repeated a number of times, when the material obtained by working between rollers is transferred into an apparently homogeneous mass in appearance much like india rubber, and which, by mixing it with sulphur, is capable of a certain degree of vulcanisation on heating.

The elasticity of this product is very small, its tensile strength not to be compared to that of india rubber; alkalies and high pressure steam saponify it. But, no doubt, for a certain number of uses this product answers as well as very low qualities of india rubber.

A very great number of preparations have been patented which are intended to serve as india rubber substitutes by themselves, and not in admixture with india rubber. So far not one of these preparations has been more than partially successful, their applicability being mostly confined to the insulation of electric conductors.

The oldest of these preparations is CALLENDER'S bitumen, which has been, and is still, largely employed for the manufacture of the larger sizes of insulated electric cables. It is a preparation very similar to the ordinary brown substitute of the rubber manufacturer, and obtained by heating a mixture of stearine pitch and sulphur under certain conditions. The electric insulation obtainable with this preparation is very low as compared with a good india rubber insulation, but its behaviour against high voltage currents is nevertheless very satisfactory. For telephone or telegraph cables this material is unsuitable, owing to its rather high inductive capacity.

Highly interesting are NOBEL'S attempts to produce 'artificial india rubber' from nitrocellulose[1] by dissolving this substance in nitro or bromonitro derivatives of certain aromatic hydrocarbons—camphor or resin oil. That 'resilient solutions' of this description could at all be employed in place of india rubber is highly improbable, but NOBEL'S idea of arriving at a rubber substitute by preparing what I termed above a 'resilient solution' of a colloid is well worth further consideration. Very probably the recent elaboration of 'Velvril,' a new substitute for india rubber and gutta percha, by W. F. REID,[2] was suggested by NOBEL'S experiments in this direction.

REID'S 'Velvril' is a solution of a nitrocellulose of a 'low degree of nitration' in a nitrated oil, preferably linseed or castor oil. The progress in this case lies in the substitution of a nitrated oil for NOBEL'S aromatic nitro-compounds, and would no doubt result in the production of a much less combustible, and probably also more 'structureless' or 'colloidal,' product than could be obtained by NOBEL'S formulæ. But whether

[1] Eng. Pat., No. 20,234, 1893; and No. 15,964, 1894.
[2] *Journ. Chem. Soc.*, 1899, p. 972.

'Velvril,' for which its inventor claims a great deal, is a really satisfactory substitute for india rubber and gutta percha requires more proof than we possess at present. *A priori* it would appear very doubtful whether a mixture of nitrated oils and nitrocellulose is a sufficiently stable product to be generally used in place of india rubber and gutta percha. It would certainly be surprising if such a mixture or solution was not greatly affected by any considerable rise or fall of temperature over and below mean atmospheric temperature.

Resins, Pitches, and Waxes.[1]

The number of different resins and waxes, or waxlike substances, and pitches which have been used in connection with rubber, or which are supposed to impart new and valuable properties to rubber goods, is almost endless. That in many cases, by the addition of one of these substances to india rubber mixings, a certain technical effect can be obtained is unquestionable, but it may, nevertheless, be safely said that the less any of these substances are used, the better for the article produced. In soft rubber goods only a very moderate use is and should be made of these substances, but hard rubber goods often contain very large proportions of resins, chiefly shellac and amber.

Perhaps the most interesting of these substances are the pitches, and more especially those which are more of a colloidal or elastic description rather than brittle. Used in moderate proportions in india rubber mixings, they certainly seem to tend to increase the resiliency of the india rubber, and to decrease its liability to deterioration by oxidation. Very valuable results may be expected from a thorough methodical study of this interesting subject, which, so far, has received scant attention only.

The analytical detection of those bodies in india rubber mixtures offers very little difficulty as far as the resins are concerned, owing to their insolubility in acetone and their solubility in alcohol. The latter offers also a ready means for their separation from waxes and pitches which are quite insoluble in alcohol. The waxes are all fairly freely soluble in acetone, but insoluble in alcohol. The pitches—boiled tar, stearine pitch—are partly soluble in acetone, and also in cold nitrobenzene, but the proportion of soluble constituents in them is by no means constant. Asphaltum and sulphuretted stearine pitch (CALLENDER's compound) are scarcely, if at all, soluble in acetone. They dissolve more or less completely in warm nitrobenzene. But it will be readily inferred from these that a satisfactory estimation of these pitches, and especially if they should occur together with resins or waxes, may occasionally be a very difficult matter. Our inabilities in this respect are, however, to a considerable extent counter-

[1] By this term only the mineral waxes—paraffin wax, ceresin, and ozokerite—are understood, but not bee's wax, the use of which offers no tangible advantage in conjunction with india rubber, although it is supposed to be used in a certain kind of 'hard rubber' (Kiel compound).

balanced by the fact that mixtures of these substances are very rarely, if ever, employed in rubber mixings; and further, it is generally quite sufficient for practical purposes to establish the presence and determine the quantities of resinous or waxy substances in an india rubber sample without finally identifying them. This, in fact, can always be done without much difficulty.

The Chemical Analysis of Organic India Rubber Substitutes.

1. **Recovered Rubber.**—The chemical analysis of recovered india rubber is carried out in exactly the same manner as the analysis of manufactured india rubber. A complete analysis, therefore, would have to account for the following items:—

(*a*) Free oils, or fats.
(*b*) Resins, waxes, pitches.
(*c*) Fatty rubber substances { S in substitute. / Cl in ,, }
(*d*) Free sulphur.
(*e*) India rubber.
(*f*) Sulphur of vulcanisation.
(*g*) Insoluble organic matter other than above named.
(*h*) Carbonaceous matter.
(*i*) Mineral constituents.

Indeed, to some extent this subject has already been dealt with in the foregoing pages. For the determination of the suitability of a given sample of recovered rubber, such a detailed analysis is generally unnecessary, and the determination of the above items (*a*), (*b*), and (*c*) under one head, (*d*), (*e*), (*f*), and again (*g*), (*h*), and (*i*) in the aggregate, will be found, in the vast majority of cases, to supply all the information required and which is obtainable by chemical analysis.

The value of a given sample of recovered india rubber depends upon two factors, of which the first represents the 'waste rubber value' of the sample, and which is, with a very fair approximation, ascertainable by analysis. The second factor consists in the 'technical effect' produced by the recovering process which is demonstrated by the plasticity of the sample, and its elasticity and tensile strength after revulcanisation.

By estimating the amount of pure rubber in a sample of recovered rubber, we are at once able to calculate the price paid for the rubber actually present. The value of the other constituents—substitute, oil, sulphur, mineral matter—is so small as to be hardly worth allowing for. It is, of course, obvious that the 'waste rubber value' should also depend upon the quality or brand of rubber present, but as yet no sufficiently reliable constants are known which would enable us to distinguish analytically between different brands of india rubber; and if there were such, the fact that rubber goods are in the vast majority of cases manufactured from a mixture of at least two different brands of rubber would go a long way to render such an estimation practically illusory. In practice,

however, this objection proves much less important as it might perhaps appear, owing to the fact that the 'technical effect' produced by the recovering process is determined not only by the efficiency of the particular process employed, but very largely also by the brand of rubber upon which it is exercised. We are not able to determine the ratio in which these two items contribute to the 'technical effect' achieved, but it is for practical purposes sufficient to determine it in its totality by examining the elasticity and tensile strength of the sample after revulcanisation.

All the commercial samples of recovered rubber, many of which are offered under very misleading descriptions, issue very badly from this efficiency test. Indeed, it may safely be said that most of them are very little more than mere bulking agents. Their chief advantage against the fatty substitutes lies in the fact that they are very much more stable than the latter, and therefore less liable to cause trouble in the manufacturing process, or when in use in the form of india rubber articles of one kind or another. That the foregoing statement is none too severe will become at once apparent if a number of commercial samples of recovered rubber are subjected to the extraction test with acetone. It will be found that all these samples yield from 6 to 14 per cent. of an extract, the greatest part of which consists of either a fatty oil, a hydrocarbon oil (both mineral and resin oils are used), or a mixture of them. The extracted rubber will now be found to have lost almost all its former plasticity, elasticity, and tensile strength, and to consist of a more or less cohering aggregate of 'crumbs' of vulcanised rubber possessing neither plasticity nor tensile strength. This shows that this kind of 'recovered' rubber is at best merely a kind of semi-solid solution of the vulcanised rubber in oil, and in the worst cases only a mass of crumbs, the cohesion amongst which is due by the stickiness produced by the combined action of heat and oil upon india rubber. In neither case could it be said that a true 'recovery' of the india rubber had been effected. All that can be claimed for such products is that they contain vulcanised india rubber in a form in which it can more satisfactorily be mixed with fresh rubber than if it was merely in the state of dry crumbs.

On submitting samples of recovered rubber of this description to the vulcanisation test, products are obtained which compare very unfavourably indeed with even the very low grades of crude rubber, and I am certainly strongly of opinion that the prices asked and paid for recovered rubber of this description are altogether out of proportion to its intrinsic value. They are, unfortunately, used at present in a very indiscriminate and uncritical manner, producing the semblance, but not giving the substance of quality, in the articles produced by their aid.

The vulcanisation test is carried out by mixing the sample to be tested in the usual way between mixing rollers with enough sulphur to make the mixed product contain 6 per cent. of free sulphur. This mixture should be calendered into a sheet of standard thickness, say $\frac{1}{8}$ or $\frac{1}{16}$ of an inch,

The sheets are then vulcanised under standard conditions. What these conditions are is not very essential as long as all the tests are made under the same conditions. The vulcanisation is effected between steam-heated plates, but personally I prefer to vulcanise in high pressure steam, as this method is certainly handier in the laboratory. In the latter case, a digestor of the construction of fig. 1 is employed. It should be capable of withstanding a working pressure of at least 150 lbs., and should be fitted with pressure gauge, thermometer tube, safety valve, and blow-off tap. Inside this digestor a cage can be inserted, the bottom of which reaches to within 2·5 inches of the bottom of the digestor. This cage receives the sample to be vulcanised, which is either secured upon a strip of glass plate or wound helically, the convolutions not touching, upon a glass cylinder of suitable size. The digestor is served with water to a height of 1·5 to 2 inches from the bottom, and the cage should certainly be clear of the surface of this water. The digestor is heated by means of a Bunsen burner. The height of the flame requires careful regulation. Even with this arrangement it will, however, still be necessary to employ a gas governor (pressure regulator) in order to keep the temperature reasonably constant. ELSTER's or STOTT's gas governors prove most satisfactory, and the first named is also the least expensive.

With regard to the temperature at which the vulcanisation is carried out, and its duration, no hard and fast rules can be suggested. These conditions may with advantage vary in different laboratories, according to the varying vulcanising conditions which are dictated by the nature of the articles manufactured. As a good average I recommend a temperature of 130° C. for from two to two and a half hours.

The vulcanised strip is cut to a standard width, say 1 inch, and its breaking strength estimated in a machine constructed upon the principle of the well-known yarn testing machine.

It is very frequently found that the amount of mechanical work required to mix certain descriptions of recovered rubber with fresh rubber, so as to produce as nearly homogeneous a 'compound' as possible, varies very considerably with different brands and grades of recovered rubber. Indeed, with some of them this result is unattainable, as the 'compound' would require an amount of working which would prove fatal to the fresh rubber employed. As a consequence, it is frequently found that 'compounds' of this description are simply colloidal agglomerates exactly as 'compounds' of rubber and oil substitutes, but generally much coarser. It will generally be observed that this phenomenon almost invariably is exhibited by those kinds of recovered rubber which pass the vulcanising test badly, or which, in other words, have been inefficiently 'recovered.' It is therefore generally advisable to put samples of recovered rubber to a mixing test, and examine the appearance of a surface cut produced with a sharp knife. A granular, spotted, or streaky section indicates a more or less heterogeneous mixture. Very characteristic for the recognition of this

defect is also the appearance of such a section after wetting it with one of the india rubber solvents : a section of a homogeneous mixture swells into a smooth surface, a section of a heterogeneous mixture becomes granular, or irregularly furrowed and indented.

2. **Fatty Substitutes.**—The fatty substitutes discussed in the earlier part of this section, which are offered in a great number of variations, are commercially divided into two classes—*viz.*, brown and white substitute—and to this division corresponds also an essential difference in their composition, colour, mode of preparation, and manner of employment.

The brown substitutes are prepared by the action of sulphur upon the triglycerides of unsaturated fatty acids at high temperatures, the white substitutes by the action of sulphur monochloride upon similar triglycerides in the cold. Accordingly, the brown substitutes represent sulphides, the white substitutes chlorosulphides of fatty oils.

The value of these substitutes lies in their chemical stability and their insolubility in solvents, which renders it possible to use them in more or less considerable quantities in rubber mixings as bulking agents, without increasing the specific gravity or reducing the suppleness of the manufactured articles.

The solubility of these substitutes can be ascertained by experiment, and is carried out by extraction with ether or acetone. The extract, after distilling off the ether, is dried for one hour at 100° C. It must, however, not be assumed that this extract, as a whole, represents dissolved substitute. Indeed, this is only true of a very small portion of it. The bulk of this extract consists of triglycerides which have not taken part in the reaction with either sulphur, or chloride of sulphur, and besides this, it always contains a sensible quantity of free sulphur.

It is obvious that the smaller the quantity of this extract, the less is a substitute likely to cause trouble in the manufacture. THOMSON [1] pointed out that the oily extracts obtained from rubber substitute do not affect india rubber detrimentally. This, no doubt, is to a large extent correct, as the oils which escape the reactions leading to these rubber substitutes are bodies which have no perceptible action upon india rubber. Moreover, their presence in the substitutes cannot altogether be avoided. But this point, nevertheless, should be made the subject of careful control in manufacturing, first with a view of keeping the percentage of soluble fatty matter in the substitute as low as possible, and further to keep this percentage as near as possible constant. That for certain purposes fatty substances are designedly added to india rubber mixings does not minimise the importance of this control, one of the chief purposes of which is to assist towards that uniformity of working conditions, without which serious break-downs in the uniformity of the manufactured goods are unavoidable.

All these substitutes contain, as has already been stated, free sulphur,

[1] *Journ. Soc. Chem. Ind.*, 1885, p. 710.

the presence of which in white substitutes is always rather small and practically irrelevant. Not so in brown substitutes, which not only reaches often rather high figures, 8 per cent. and more, but is, moreover, apt to vary considerably. As brown substitutes are used exclusively for dry heat cured goods, the knowledge of the exact amount of free sulphur in the substitute becomes an important matter, and the neglect of this obvious precaution is a fruitful cause of many vulcanising troubles.

The determination of the free sulphur is best carried out in conjunction with the determination of the soluble fatty matter. The extraction of the substitute may be carried out with ether, but acetone is to be preferred as being a better solvent for sulphur. Carbon bisulphide might perhaps appear the most suitable solvent to employ, but, as a matter of fact, it cannot be used, as it always dissolves from the substitute a small quantity of organic matter which cannot be readily separated from the free sulphur. Accordingly we proceed in this manner, that from 3 to 5 grms. of the finely ground substitute are weighed out in one of the paper tubes, closed at one end, which are much used in milk analysis. The open end of this tube is then lightly closed by inserting into it a small tuft of fat-free cotton wool, transferred to a Soxhlet extractor, and extracted for at least four hours with acetone, the extract being received in a weighed flask. After extraction the acetone is completely distilled off. The extract thus obtained is now treated with 20 c.c. of acetone to redissolve the organic matter when the free sulphur separates out as a crystalline mass. The fatty matter being completely dissolved, the solution is filtered through a small filter into another weighed flask, care being taken to retain the precipitated sulphur as much as possible in the first flask. The latter is then washed three times with 5 c.c. of cold acetone, all the washings being successively filtered into the second flask. Finally, the small filter is carefully washed with another 5 c.c. of acetone. The filter is then removed to the first flask, and 10 to 15 c.c. of carbon bisulphide are filtered through it into the first flask. Any sulphur which was poured into this filter in the first washings will thus be dissolved. The contents of both flasks are now evaporated to dryness, and dried for one hour at 100° C. If the operation has been properly conducted, the first flask will be found to contain a number of globules of pure sulphur,[1] the second a clear, semi-fluid, fatty substance. The amount of each is determined by weighing.

The figures so obtained are satisfactorily accurate for ordinary purposes, but occasionally it may appear desirable to apply to them a correction on account of the solubility of sulphur in cold acetone, which amounts to 0·06 per cent. at a temperature of 18° C. Accordingly, the 40 c.c. of acetone used in separating the sulphur and fatty matter would dissolve 0·020 grms. of sulphur. To correct the figures we would therefore have

[1] These remain liquid for a long time, but crystallise instantly on being touched with a glass rod.

to deduct this amount[1] from the amount of fatty matter present, and add it to the quantity of sulphur as ascertained by weight.

These figures already afford a very satisfactory criterion by which to judge the identity of the quality of successive deliveries. In doubtful cases, however, or when it becomes necessary to decide as to the identity or otherwise of samples from different sources, the determination of the combined sulphur, or of combined sulphur and chlorine, in the case of white substitutes should not be omitted. To employ for this purpose the substitute in its ordinary condition—*i.e.*, to determine the total sulphur in it, and then put the combined sulphur as the difference between this total sulphur and the amount of free sulphur previously ascertained—is, however, not permissible. The reason for this objection lies in the fact that the fatty extract always also contains a certain amount of combined sulphur which cannot properly be considered to represent sulphur present in the form of insoluble substitute. For this reason the combined sulphur should be determined in the extracted sample of substitute after drying.

For this purpose 1 grm. of the extracted substitute is treated according to HENRIQUES' method for the determination of the total sulphur in india rubber fully described on page 253. The amount of free sulphur should be calculated, not upon the extracted, but upon the unextracted, substitute.

The above data—soluble fatty matter, free sulphur, combined sulphur—suffice, in the vast majority of cases, to decide the question of conformity to standard of samples of substitute, white or brown, and also to judge their quality in general as far as chemical analysis can decide this point. Regarding this, it may be taken that a white substitute containing not more than 10 per cent. of soluble fatty matter and not less than 8 per cent. of combined sulphur, or a brown (black) substitute containing not more than 5 per cent. of soluble fatty matter, and the amount of free sulphur in which does not exceed 40 per cent. of the amount of the combined sulphur, are, from the chemical point of view, safe to use. It should, however, always be remembered that these figures represent higher limits—at any rate, as far as the percentages of soluble fatty matter are concerned.

There are also, however, some technological points in connection with these substitutes of which the analyst should take note. It is quite feasible that a sample of substitute may in every respect come up to our analytical standard and nevertheless prove unsatisfactory with regard to the mixture it forms with the india rubber between the mixing rollers. This mixture should be so fine, that on pulling part of it into a transparent skin, no appearance of structure, due to microscopic particles or flakes of substitute, should be observable. The skin should have the appearance of an opalescent or turbid medium. Under the microscope a thin film should present the image of fig. 8, and not of fig. 9. And this result

[1] It is scarcely necessary to point out that it would be useless to carry this correction beyond the first decimal.

should be arrived at without the mixture requiring an amount of working detrimental to the india rubber.

The microscopic preparations of such mixings are obtained by dissolving a small quantity of the latter in sufficient benzene to produce a solution of the consistency of thin honey. A very small drop of this solution is placed upon one end of a micro slide, and by drawing another micro slide rapidly across this drop, an extremely thin rubber-substitute film is produced, which, after a few moments' drying, is ready for observation. In permanent preparations no mounting media should be used, or only such as possess a very low refractive index.

It is further advisable to test the behaviour of both white and brown substitutes against high pressure steam at vulcanising temperatures applied for three hours. Substitutes of apparently closely similar chemical composition not infrequently behave very differently in this test, some standing it very satisfactorily, others suffering more or less pronounced decomposition.

Substitutes, whether white or brown, manufactured from oxidised (blown) oils contain considerably less chlorine and sulphur, or sulphur, than substitutes manufactured from the natural oils. Thus, the brown substitutes I. and II. quoted on page 144 have been manufactured from blown colza oil, and No. III. from ordinary refined maize oil. Likewise, the white substitutes A and B in HENRIQUES' table (page 147) have been manufactured from blown or oxidised oils, and C from a natural oil. But while brown substitutes produced from blown oils are at least as satisfactory as those obtained from natural oils, and for some purposes distinctly superior, the same is not true for white substitutes prepared from blown oils. These exhibit a distinct lack of stability as compared with the normal products.

3. **Resins, Pitches, and Waxes.**—The analysis of these substances is a very simple operation.

The *resins* which are employed in the manufacture of india rubber goods are very few. The most important are colophony and shellac. The low price of colophony renders an adulteration of it a practical impossibility. Shellac, owing to its much higher price, is much more liable to be tampered with. It is stated that adulterations of this resin with colophony have been observed. These can readily be discovered by the solubility of pure shellac in ether, in which colophony is practically insoluble.

The *pitches* used in the rubber manufacture are coal tar pitch, stearine pitch, and asphaltum. *Coal tar pitch* is prepared by boiling the liquid coal tar until it has reached such a consistency that it sets just hard, but not brittle, on cooling. At least 90 per cent. of it should be soluble in boiling benzene.

Stearine pitch, the origin of which is sufficiently indicated by its name, varies very greatly in its composition and appearance. It occurs sometimes as a very sticky, almost treacly mass; sometimes it forms hard,

brittle pieces; but the only form in which it is satisfactory to use is in the form of a coherent semiplastic mass. It is by no means a homogeneous body, but consists of a part soluble in ether, acetone, and benzene, and of another part which is insoluble in all solvents. The soluble part consists practically entirely of fluorescent hydrocarbons, and should contain no saponifiable matter. The insoluble part is a black carbonaceous mass. Its amount should not exceed 20 per cent., but often forms as much as 60 per cent. of the product.

Asphaltum is not extensively used, and the products in the market under this name differ very greatly in composition and properties. The quality generally used in rubber works is that known as Syrian or Judea Asphaltum. Only from 4 to 5 per cent. of it should be soluble in alcohol. From 40 to 50 per cent. should be soluble in ether, and the whole in chloroform, turpentine, and nitrobenzene.

Practically the only waxes used in connection with india rubber are paraffin wax, and ceresin or ozokerite. The quality of these products is expressed by their melting points, which for paraffin wax ranges from about 28 to 53° C., and for ceresin from 70 to 76° C. Adulterations of paraffin wax are scarcely feasible, but adulterations of ceresin with resin (colophony) are by no means uncommon. This is, however, easily detected by the solubility of resin in 60 per cent. strong alcohol, in which ceresin is entirely insoluble. The quantitative determination of this adulteration is carried out by boiling 2 grms. of the ceresin with 20 c.c. of alcoholic caustic soda (6 per cent.) for twenty minutes on a reflux condenser. The ceresin hydrocarbon is then allowed to solidify by cooling, when the alcoholic solution is poured into a dish, the flask with the ceresin rinsed several times with small quantities of alcohol, and the washings added to the alcoholic solution. This solution is then evaporated to dryness, the residue again taken up with boiling water, slightly acidulated with hydrochloric acid, and again evaporated to dryness. The free resin is now separated from the sodium chloride present by dissolving it in alcohol, evaporating to dryness, and weighing the residue. Or the weight of the first obtained mixture of resin and sodium chloride is ascertained, the whole then ignited, and the weight of the residual sodium chloride determined. The calculation of the amount of resin present is obvious.

CHAPTER IV.

INORGANIC COMPOUNDING MATERIALS.

THE inorganic compounds used in india rubber mixings serve a number of purposes, and their suitability must be considered, therefore, from the point of view of the particular effect aimed at by their employment.

Foremost stand the compounds used as filling or bulking agents, the chief purpose of their employment being to reduce the price of the manufactured article. Next in importance stand the substances acting as 'sulphur carriers,' and the effect of which is either to hasten, or else to modify, the vulcanisation in certain ways. Lastly, there are a number of compounds which are employed to give the manufactured article some definite colour. It must not, however, be assumed that there exists a sharp line of division between the compounds of one group and those of the other two. Most of the filling agents more or less distinctly influence the vulcanisation; some of the sulphur carriers might perhaps be employed as much for bulk-giving purposes as on account of their colouring properties. The above division into three groups is therefore in some cases somewhat arbitrary, but this objection is scarcely of sufficient weight to sacrifice to it the obvious advantages of the classification. In the present section we shall only deal with those inorganic compounds which are chiefly used as bulking or filling agents.

It is almost needless to say that all filling materials to be used in india rubber should be chemically absolutely inert substances; they should not be appreciably affected by temperatures of from 180 to 200° C., and their solubility in water should be very slight—practically *nil*. That they should be free from impurities deleterious to india rubber goes without saying, but any danger in this respect is very remote. This makes it evident that the chemical points in relation to inorganic compounding materials are of a very simple description, calling rarely, if ever, for more than the most elementary chemical tests. The selection of the material to be employed for some particular mixing is, indeed, in the first instance more a matter of certain physical considerations than of chemical ones—in other words, the inorganic material to be 'compounded' with the india rubber is, in the vast majority of cases, selected simply on account of the physical

properties it confers upon the manufactured article. This is exactly as we should expect, considering that the vast majority of india rubber goods are subjected to physical wear only; but it is, at the same time, obvious that in the manufacture of india rubber goods intended for use in chemical operations, the selection of the particular inorganic compounding material to be employed must primarily be influenced by the nature of the chemical influences to which the goods would be subjected when in use, and only such compounding materials should be used which behave as entirely indifferent substances under the chemical influences in question.

Perhaps the most obvious effect of mineral 'compounding materials' in india rubber is their influence upon the specific gravity of the manufactured article. Indeed, this is so pronounced that the specific gravity of such an article is in certain circles still looked upon as a reliable criterion by which to judge its quality. Of course, I need hardly point out that the extensive employment of 'substitutes' has rendered this criterion largely illusory. Nevertheless, a high specific gravity is scarcely, if ever, looked upon as a recommendation in manufactured india rubber, and for this reason the choice of a particular compounding material is often dictated by the consideration of this point. Since, however, the addition of these inorganic bodies is chiefly made with a view of cheapening the manufactured product —in other words, to gain weight—it should be pointed out that the deterioration of quality caused in manufactured rubber by such addition is not merely a matter of their absolute weight, but also of their bulk. The greater this latter, the greater the deterioration of quality in the product, so that on this account it would appear preferable to produce a desired increase in weight by using a compounding material of high specific gravity and small bulk, rather than one of low gravity and therefore large bulk, although it could not be said that this is the general practice in rubber factories. It must, however, be admitted that in cases where the article to be manufactured is intended to resist shocks (stability) rather than tension, a compounding material of smaller specific gravity is often to be preferred.

The specific gravities of the more generally used inorganic compounding materials are as follows:—

Material.	*Specific Gravity.*	*Material.*	*Specific Gravity.*
Whiting, $CaCO_3$, ...	2·7–2·9	Litharge, PbO, . . .	9·3
Plaster of Paris, $CaSO_4$, .	2·9	White lead, $3PbO.2CO_2.H_2O$,	6·1–6·2
Gypsum, $CaSO_4,2H_2O$, . .	3·2	Lead sulphate, $PbSO_4$, .	6·1–6·2
Barytes, $BaSO_4$, ...	4·3–4·6	Silica, SiO_2 (Infusorial earth),	1·66–1·95
Magnesia, MgO, ...	3·2–3·6	Lithopone, $ZnS + BaSO_4$, .	3·6–4·1
Magnesium carbonate, $MgCO_3$,	2·8–3·1	French chalk, $Mg_3Si_4O_{12}H_2$,	
Zinc oxide, ZnO, ...	5·6	China clay, $Al_2Si_2O\,H_4$, .	
Asbestos (Magnesium—Calcium silicate), ...			

It should, however, be pointed out that the physical constants shown by manufactured india rubber containing any of the above materials are by no

means simply a function of the specific gravity of the latter. This, indeed, is only true of the specific gravity of the manufactured article. All the other constants vary in a manner which bears no relation to the specific gravity of the inorganic compounding materials used, and the cause of these variations is entirely unknown. It is most probably closely connected with the physical state or structure of these compounding materials.

This matter is one of very considerable importance. A most valuable contribution on this point we owe to HEINZERLING and PAHL.[1] These authors prepared a large number of rubber mixings with a considerable variety of inorganic and organic admixtures, and submitted these samples after vulcanisation to a series of chemical tests, the tabulated results of which are reproduced *in extenso* below.

All the samples were subjected to the following tests:—

Sulphuric Acid.—The weighed samples were immersed in sulphuric acid of sp. gr. 1·1562 at ordinary temperature. After immersion they were dried, weighed again, and the changes which had taken place during immersion noted. For samples I. to XVIII., the time of immersion was 20 days; for samples XIX. to XXXII., 10 days.

Acetic Acid.—An acid of sp. gr. 1·0584 was used. The immersion was only continued for 3 days, the action of this acid being much more rapid.

Caustic Soda.—A solution of sp. gr. 1·3084 was employed and allowed to act during 3 days. The weights and specific gravities of the samples before and after treatment were observed, as also in the case of the acetic acid and ammonia.

Ammonia.—A solution of sp. gr. 0·9775 was allowed to act during 4 days.

Samples I. to XVIII. were washed after treatment with the above solutions, and dried for 6 hours at 100° C.; samples XIX. to XXXII. were, without washing, exposed to the air for 48 hours, and subsequently dried at 100° C. for 30 minutes.

Colza Oil of sp. gr. 0·9102 was used, and the samples immersed in it during 5 days. In these, as also in the two following tests, the specific gravities of the samples before and after immersion were determined.

Mineral Oil.—A lubricating oil of sp. gr. 0·8991 was employed. Time of immersion 5 days.

A mixture of 90 per cent. of *mineral oil* and 10 per cent. of *tallow* was allowed to act upon the samples during 5 days at 100° C.

[1] *Verhandl. d. Vereins z. Beförd. d. Gewerbefl.*, Berlin, 1891-92.

To test the action of *illuminating gas* upon the samples, the latter were during 20 days inserted in a tube through which the gas was passing to a burner.

Changes of volume were determined by means of a micrometer capable of indicating 0·01 mm.

The tensile strength was determined by means of a machine similar to those used for the determination of the strength of textile fabrics. The samples used for this purpose were 2 cm. long, 0·5 cm. wide, and 2 mm. in thickness.

The changes of form were determined by means of a machine similar to those used for making crushing tests on building materials, and the samples were subjected to a compression of 4·9 kilos per square centimetre during one minute. The change in thickness of the samples under this test was determined by means of the micrometer.

The changes of form under the influence of repeated shocks were determined by subjecting the samples to 50 blows of a hammer of 2 kgms. weight, falling each time through a height of 0·25 m.

The nature of the deformations caused by steady pressure and by hammering respectively may be gleaned from the following figures A (crushed) and B (hammered):—

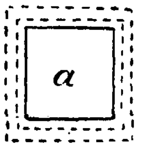

FIG. A.

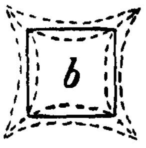

FIG. B.

The tests of the behaviour of the samples against heat were carried out in an oven provided with a glass door, so that they were under observation all the time. The temperature was raised 10° C. every half hour until 150° C. had been reached.

The electric insulation resistance was ascertained by means of WEBER'S electrometer. The samples were all heated for half an hour before being tested.[1]

[1] The above particulars of tests, as well as the following tables and conclusions, have been translated from SEELIGMANN'S French translation of the German original, which, in spite of many efforts, was inaccessible to me. For this reason I can only vouch for the conformity of my own with Seeligmann's translation.

[TABLES.

Chemical Tests.

A.—Samples prepared to Author's Instructions.						Observations.	Action of H_2SO_4. Modifications in Weights per cent.	Action of $C_2H_4O_2$. Modifications per cent.	
No.	Pará per cent.	Sulphur per cent.	Quantity and Nature of Admixtures.		Specific Gravity.			In Volumes.	In Weights.
I.	90	10	0	...	0·999	All these samples were cured for 1 hour at a temperature of from 135 to 138° C., and at a pressure of from 45 to 53 pounds.	-4·259	+ 2·912	+ 0·932
II.	85	5	10	Golden sulphide, .	1·070		-3·099	+ 2·985	+ 2·097
III.	75	5	20	Golden sulphide, .	1·101		-3·521	+ 3·846	+ 3·048
IV.	80	10	10	Zinc oxide, . .	1·087		-3·274	+ 4·854	+ 29·132
V.	50	10	40	Zinc oxide, . .	1·283		-2·074	+28·155	+153·035
VI.	10	10	80	Zinc oxide, . .	1·514		-1·810	+27·868	+116·950
VII.	80	10	5 5	Zinc oxide, . Chalk, . . .	1·184		-2·930	+ 5·357	+ 30·887
VIII.	50	10	20 20	Zinc oxide, . Chalk, . .	1·255		-2·280	+28·828	+131·899
IX.	10	10	40 40	Zinc oxide, . Chalk, . .	1·452		-1·802	+29·464	+160·097
X.	50	10	20 20	Zinc oxide, . Fluor spar, .	1·295		-1·464	+17·475	+ 62·616
XI.	10	10	40 40	Zinc oxide, . Fluor spar, .	1·502		-1·527	+31·730	+124·539
XII.	50	10	20 20	Zinc oxide, . Litharge, .	1·340		-1·864	+12·765	+ 78·542
XIII.	10	10	40 40	Zinc oxide, . Litharge, .	1·569		-1·406	+23·711	+ 77·411
XV.	50	10	40	Brown substitute, .	1·053		-4·081	*n.c.*	+ 0·560
XVI.	30	10	60	Brown substitute, .	1·052		-2·473	*n.c.*	+ 2·180
XVII.	50	10	40	White substitute, .	1·054		-6·076	+ 1·709	+ 6·378
XVIII.	30	10	60	White substitute, .	1·031		-6·306	+ 2·970	+ 8·695
XIX.	87	10	3	Magnesia, . .	1·130		-0·932	+ 4·231	+ 18·718
XX.	87	10	3	Slaked lime, . .	1·027		-0·924	+ 4·273	+ 6·297
XXI.	75	10	15	Paraffin wax, .	1·075		-4·806	+ 5·063	- 0·354
XXII.	65	10	25	Paraffin wax, .	1·041		-3·278	+ 2·197	- 0·674
XXV.	75	10	15	Turpentine, . .	1·030		-3·367	*n.c.*	+ 2·732
XXVI.	65	10	25	Turpentine, . .	1·065		-3·582	*n.c.*	+ 6·442
XXVII.	85	10	5	Glycerine, . .	1·062		-5·921	*n.c.*	- 0·420
XXVIII.	80	10	10	Glycerine, . .	1·060		-6·571	*n.c.*	+ 2·400
XXIX.	80	10	10	Bitumen, . .	1·080		-3·686	+ 1·980	+ 0·650
XXX.	70	10	20	Bitumen, . .	1·085		-2·421	*n.c.*	- 0·607
XXXI.	60	10	30	Ground rubber waste,	1·101		-2·336	*n.c.*	+ 0·332
XXXII.	80	10	60	Ground rubber waste,	1·101		-3·889	+ 1·769	+ 0·729
IA.	English cut sheet cold cured.	5	...	...	0·925		-1·344	*n.c.*	*n.c.*

n.c. No change.

Chemical Tests.

No.	Action of NaOH. Modifications per cent.		Action of NH_3. Modifications per cent.		Action of Colza Oil. Modifications in Volumes per cent.	Action of Mixture of Mineral Oil, 90 per cent.; Tallow, 10 per cent. Modifications in Volumes per cent.	Action of Mineral Oils. Modifications in Volumes per cent.	Action of Coal Gas. Modifications in Weights per cent.
	In Volumes.	In Weights.	In Volumes.	In Weights.				
I.	*n.c.*	−4·354	*n.c.*	−0·727	+23·214	*	+42·718	+ 9·765
II.	*n.c.*	−4·354	*n.c.*	−0·974	+20·617	+53·846	+39·694	+ 9·156
III.	*n.c.*	−4·271	*n.c.*	−0·896	+28·431	+34·615	+51·485	+ 7·561
IV.	*n.c.*	−2·871	*n.c.*	−0·326	+25·242	+21·782	+39·428	+11·079
V.	*n.c.*	−0·084	*n.c.*	−0·314	+32·110	+58·878	+43·519	+10·085
VI.	*n.c.*	−0·087	*n.c.*	−0·779	+47·272	+78·947	+36·440	+ 7·674
VII.	*n.c.*	−2·824	*n.c.*	−0·629	+24·137	+65·765	+40·178	+10·868
VIII.	*n.c.*	−2·059	*n.c.*	−0·856	+37·247	+77·570	+46·296	+ 7·370
IX.	− 0·892	−1·422	*n.c.*	−0·707	+27·193	+65·853	+35·593	+ 5·821
X.	− 1·000	−3·348	*n.c.*	−0·455	+28·853	+51·923	+40·384	+ 8·549
XI.	*n.c.*	−2·160	*n.c.*	−0·512	+28·571	+65·048	+41·121	+ 1·452
XII.	*n.c.*	−1·158	*n.c.*	−0·011	+37·894	+53·763	+38·613	+10·048
XIII.	*n.c.*	−0·282	*n.c.*	−0·388	+28·712	+57·916	+30·000	+ 8·695
XV.	− 1·388	−5·745	*n.c.*	−0·787	+21·428	*	+50·714	+11·793
XVI.	*n.c.*	−4·965	− 3·571	−0·744	+20·339	*	+32·773	+14·047
XVII.	− 7·017	−9·723	−1·724	−2·147	+11·111	*	+44·545	+ 7·574
XVIII.	− 9·708	−9·658	−1·941	−1·649	+14·423	*	+55·445	+ 7·987
XIX.	*n.c.*	−1·321	*n.c.*	−0·247	+ 6·250	*	+36·440	+10·143
XX.	− 0·847	−6·569	*n.c.*	−0·327	+18·487	*	+29·752	+10·043
XXI.	−10·588	−5·602	*n.c.*	−1·722	+23·595	*	+43·750	+12·758
XXII.	− 7·692	−4·847	*n.c.*	−2·882	+10·000	*	+35·781	+13·581
XXV.	*n.c.*	−5·210	*n.c.*	+0·239	+20·491	*	+39·603	+10·368
XXVI.	*n.c.*	−5·961	*n.c.*	+0·496	+26·732	*	+31·460	+11·382
XXVII.	− 5·940	−7·628	*n.c.*	+0·309	+23·904	*	+48·214	+11·618
XXVIII.	− 3·846	−7·992	*n.c.*	+3·909	+21·551	*	+45·794	+ 8·905
XXIX.	*n.c.*	−4·382	*n.c.*	+0·121	+10·434	+73·684	+45·714	+12·514
XXX.	*n.c.*	−3·425	*n.c.*	+0·225	+17·647	+75·757	+40·740	+11·248
XXXI.	− 2·849	*n.c.*	*n.c.*	+0·718	+14·150	*	+58·846	+10·810
XXXII.	− 0·883	−3·473	+0·869	−2·081	+15·781	*	+47·000	+ 5·807
IA.	*n.c.*	*n.c.*	*n.c.*	+1·592	+28·461	*	+54·198	+15·121

n.c. No change. * These samples dissolved entirely.

Physical Tests.

A.—Samples prepared to Author's Instructions.

No.	Pará per cent.	Sulphur per cent.	Quantity and Nature of Admixtures.		Specific Gravity.	Observations.	Modulus of Pressure per 1² mm.	Modulus of Resistance per 1² mm.	Distensibility in mm. per 100 mm.
							grms.	grms.	
I.	90	10	0	...	0·999	All these samples were cured for 1 hour at a temperature of from 135 to 138° C., and at a pressure of from 45 to 53 pounds.	48·5	213	1100
II.	85	5	10	Golden sulphide, .	1·070		38·0	213	790
III.	75	5	20	Golden sulphide, .	1·101		47·5	259	850
IV.	80	10	10	Zinc oxide, . .	1·087		48·5	427	825
V.	50	10	40	Zinc oxide, . .	1·283		47·5	480	725
VI.	10	10	80	Zinc oxide, . .	1·514		43·5	543	660
VII.	80	10	5 5	Zinc oxide, . . Chalk, . .	1·184		46·0	440	760
VIII.	50	10	20 20	Zinc oxide, . . Chalk, . . .	1·225		65·0	542	710
IX.	10	10	40 40	Zinc oxide, . . Chalk, . . .	1·452		69·0	653	665
X.	50	10	20 20	Zinc oxide, . . Fluor spar, . .	1·295		48·0	404	660
XI.	10	10	40 40	Zinc oxide, . . Fluor spar, . .	1·502		77·5	563	640
XII.	50	10	20 20	Zinc oxide, . . Litharge, . .	1·340		31·5	404	490
XIII.	10	10	40 40	Zinc oxide, . . Litharge, . .	1·569		31·0	352	305
XV.	50	10	40	Brown substitute, .	1·053		22·5	220	750
XVI.	30	10	60	Brown substitute, .	1·052		22·5	77	360
XVII.	50	10	40	White substitute, .	1·051		16·0	66	600
XVIII.	30	10	60	White substitute, .	1·031		15·0	55	455
XIX.	87	10	3	Magnesia, . .	1·130		70·5	427	465
XX.	87	10	3	Slaked lime, . .	1·027		45·0	225	665
XXI.	75	10	15	Paraffin wax, . .	1·075		15·0	109	830
XXII.	65	10	25	Paraffin wax, . .	1·041		14·0	115	1025
XXV.	75	10	15	Turpentine, . .	1·030		15·0	96	825
XXVI.	65	10	25	Turpentine, . .	1·065		12·0	51	630
XXVII.	85	10	5	Glycerine, . .	1·062		29·9	376	975
XXVIII.	80	10	10	Glycerine, . .	1·060		25·5	365	1050
XXIX.	80	10	10	Asphaltum, . .	1·080		45·0	342	950
XXX.	70	10	20	Asphaltum, . .	1·085		67·5	407	875
XXXI.	60	10	30	Ground rubber waste,	1·101		29·0	178	650
XXXII.	30	10	60	Ground rubber waste,	1·101		25·5	156	600
IA.	English cut sheet cold cured.	5	...	...	0·925		38·5	230	772

Physical Tests.

No.	Change of Form under the Influence of Strong Compression. Initial Thickness.	Thickness of Swelled Edges.	Thickness at Centre.	Stretch of Extreme Edges.	Change of Form under the Influence of a Succession of Blows. Initial Thickness.	Thickness of Swelled Edges.	Thickness at Centre.	Stretch of Extreme Edges.	Insulating Power. Observed Depressions.	Action of Heat.
	mm.	mm.	mm.	mm.	mm.	mm.	mm.	mm.		
I.	0·95	1·18	0·93	9·00	0·95	1·54	0·71	2·75	117	Normal.
II.	1·36	1·48	1·27	9·00	1·31	1·68	1·03	4·50	12	,,
III.	1·08	1·16	1·01	8·25	1·10	1·40	0·09	5·00	6	,,
IV.	1·01	1·07	0·98	9·50	1·00	1·31	0·82	4·50	171	,,
V.	1·12	1·15	1·10	9·50	1·09	1·40	0·91	4·75	123	,,
VI.	1·17	1·20	1·11	9·50	1·11	1·35	0·99	5·50	4	,,
VII.	1·05	1·15	1·01	9·00	1·05	1·30	0·91	4·25	4	,,
VIII.	1·09	1·20	1·02	9·00	1·02	1·28	0·90	4·75	4	,,
IX.	1·14	1·21	1·03	9·00	1·13	1·56	0·95	5·00	3·5	,,
X.	0·98	1·02	0·91	9·00	1·00	1·42	0·82	4·75	2	,,
XI.	1·03	1·07	0·95	9·00	1·09	1·26	0·98	4·50	3·5	,,
XII.	0·94	0·89	0·85	8·25	0·93	1·15	0·82	3·50	225·7	,,
XIII.	0·91	0·84	0·86	8·00	0·91	1·19	0·78	4·00	220·5	,,
XV.	0·85	0·96	0·75	6·50	0·78	1·22	0·67	4·75	9	Vapours on raising temperature.
XVI.	1·19	incommensurable	0·92	4·25	1·15	1·21	0·91	5·00	2	,,
XVII.	0·96	1·20	0·84	5·50	1·02	1·05	0·73	3·75	50	,,
XVIII.	1·00	1·29	0·91	incommensurable	0·94	0·96	0·64	4·50	222	,,
XIX.	1·04	1·08	1·03	10·00	1·01	1·26	0·91	4·50	7·5	Normal.
XX.	1·23	1·35	1·06	8·50	1·21	1·55	0·96	3·25	9·5	,,
XXI.	0·91	1·13	0·78	7·50	1·21	1·55	0·96	3·25	1	Vapours on raising temperature.
XXII.	1·15	1·20	1·01	7·25	1·11	1·45	0·77	5·75	0	,,
XXV.	1·06	1·25	0·97	8·50	1·16	1·54	1·01	3·25	1·5	Vapours at higher temperatures.
XXVI.	1·02	1·21	0·91	8·50	1·09	1·26	0·82	4·00	1·5	,,
XXVII.	1·07	1·41	1·00	7·75	1·03	1·64	0·93	4·25	3	,,
XXVIII.	1·14	1·35	1·03	8·00	1·16	1·92	0·92	2·50	5	,,
XXIX.	1·25	1·92	1·15	4·50	1·28	1·06	1·06	8·75	2	Normal.
XXX.	1·07	1·42	0·95	3·50	1·08	0·90	0·90	2·00	2	,,
XXXI.	1·04	1·35	0·91	2·50	1·03	0·91	0·91	2·75	3·5	,,
XXXII.	1·25	1·44	1·17	4·50	1·42	1·08	1·08	4·00	1·5	,,
Ia.	1·38	1·88	1·25	10·00	1·38	1·29	1·29	7·75	2·22	,,

Chemical Tests.

B.—Commercial India Rubber Articles.							Action of H_2SO_4. Modifications in Weights per cent.	Action of $C_2H_4O_2$. Modifications per cent.	
No.	India Rubber per cent.	Sulphur per cent.	Quantity and Nature of Admixtures.		Spec. Grav. after Manufacture.	Spec. Grav. after 2½ Years.		Volumes.	Weights.
1	91	9	0	...	0·990	0·999	+ 0·583	+ 0·714	+ 2·540
2	82	8	10	Chalk, . . .	1·100	1·111	+ 0·998	+19·083	+37·688
3	43	5	7 45	Brown substitute, . Zinc oxide, . .	1·400	1·490	+ 0·402	+34·259	+51·319
4	47	7	27 16	Chalk, . . . Zinc oxide, . .	1·400	1·500	− 1·427	+46·216	+81·790
5	66	0	16 9 9	Golden sulphide, . Chalk, . . . Zinc oxide, . .	1·200	1·304	− 0·665	+42·975	+90·209
6	70	7	23	Chalk, . . .	1·165	1·222	− 0·830	+37·190	+72·947
7	92	0	8	Metal,[1] . . .	0·999	1·111	− 1·168	+ 2·205	+26·263
8	71	7	16 6	Chalk, . . . Zinc oxide, . .	1·450	1·660	− 0·832	+ 9·278	+53·321
9	58	0	6 30 5 1	Brown substitute, . Chalk, . . . Metal,[1] . . . Paste,[1] . . .	1·215	1·330	− 0·532	+ 7·627	+78·623
10	36	6	4 27 27	Brown substitute, . Chalk, . . . Zinc oxide, . .	1·550	1·720	− 0·159	+19·841	+11·298
11	31	6	6 15 40 2	Brown substitute, . Chalk, . . . Zinc oxide, . . Paste,[1] . . .	1·600	1·806	− 0·859	+21·481	+13·589
12	39	0	4 10 3 3 0·5 32 8	Brown substitute, . Chalk, . . . Zinc oxide, . . Metal,[1] . . . Paraffin wax, . Fluor spar, . . Mixture,[1] . .	1·650	1·920	+ 1·303	+15·126	+31·422
13	22	0	8 52 0·5 0·5 11 6	Golden sulphide, . Chalk, . . . Paraffin wax, . Paste,[1] . . . Recovered rubber, . Brown substitute, .	*n.c.*	1·760	+23·443	+17·355	+21·078
14	30	0	40 25 3 2	Chalk, . . . Zinc oxide, . . Metal,[1] . . . Paste,[1] . . .	*n.c.*	1·903	+ 5·824	+21·705	+15·703
15	20	0	18 3 2 35 12	Chalk, . . . Metal,[1] . . . Paste,[1] . . . Fluor spar, . . Lead oxide, . .	*n.c.*	2·041	+41·666	+21·538	+15·228

[1] For further information on these compounds, *see* page 174. *n.c.* No change.

Chemical Tests.

No.	Action of NaOH. Modifications per cent. Volumes.	Action of NaOH. Modifications per cent. Weights.	Action of NH_3. Modifications per cent. Volumes.	Action of NH_3. Modifications per cent. Weights.	Action of Colza Oil. Modifications in Volumes per cent.	Action of Mineral Oils. Modifications in Volumes per cent.	Action of Mixture of Mineral Oil, 90 per cent. ; Tallow, 10 per cent. Modifications in Volumes per cent.	Action of Coal Gas. Modifications in Weights per cent.
1	*n.c.*	− 1·934	*n.c.*	+ 1·503	+18·045	+36·641	+89·312	+12·431
2	*n.c.*	− 2·332	+ 3·937	+ 3·357	+ 6·666	+23·664	+70·992	+12·139
3	*n.c.*	− 3·058	+ 0·482	+ 4·309	+47·663	+31·428	+84·955	+ 6·027
4	*n.c.*	− 1·847	+ 4·001	+ 4·722	+ 3·708	+10·077	+55·118	+ 5·596
5	*n.c.*	− 0·564	+16·071	+ 2·877	+ 6·140	+12·931	+ 7·692	+ 8·271
6	*n.c.*	− 1·534	+ 5·660	+ 6·600	+ 5·737	+12·068	+18·333	+ 8·059
7	−1·470	− 1·266	+11·450	+23·550	*n.c.*	+ 8·450	+34·677	+ 8·413
8	*n.c.*	− 1·600	+15·217	+17·652	+ 6·382	+18·556	+54·347	+ 4·836
9	*n.c.*	− 4·650	+10·250	+22·405	*n.c.*	+ 5·024	+13·559	+ 4·133
10	*n.c.*	−19·083	+ 6·299	+ 6·863	+27·480	+30·708	+81·679	+ 4·494
11	−0·699	−20·551	+ 4·347	+ 6·238	+20·595	+21·428	+64·492	+ 5·069
12	*n.c.*	−14·724	+ 7·438	+ 6·009	+27·168	+22·413	incommensurable	+ 5·843
13	*n.c.*	− 1·601	+ 9·090	+ 8·391	+15·125	+14·876	+47·580	+ 4·020
14	*n.c.*	− 1·655	+10·156	+ 8·665	+ 7·031	+ 8·064	+33·343	+ 3·837
15	*n.c.*	− 0·163	+ 6·666	+ 6·474	+10·687	+11·627	+27·480	+ 3·122

n.c. No change.

Physical Tests.

B.—Commercial India Rubber Articles.							Modulus of Pressure per 1² mm.	Modulus of Resistance per 1² mm.	Distensibility in mm. per 100 mm.
No.	India Rubber per cent.	Sulphur per cent.	Quantity and Nature of Admixtures.		Spec. Grav. after Manufacture.	Spec. Grav. after 2½ Years.	grms.	grms.	
1	91	9	0	...	0·990	0·999	33·5	201	675
2	82	8	10	Chalk,	1·100	1·111	40	230	600
3	43	5	7 45	Brown substitute, Zinc oxide,	1·400	1·490	21	349	580
4	47	7	27 16	Chalk, Zinc oxide,	1·400	1·500	38·5	124	160
5	66	0	16 9 9	Golden sulphide, Chalk, Zinc oxide,	1·200	1·304	43	173	235
6	70	7	23	Chalk,	1·165	1·222	15	86	190
7	92	0	8	Metal,[1]	0·999	1·111	16	25	110
8	71	7	16 6	Chalk, Zinc oxide,	1·450	1·660	31·5	63	145
9	58	0	6 30 5 1	Brown substitute, Chalk, Metal,[1] Paste,[1]	1·215	1·330	12	33	110
10	36	6	4 27 27	Brown substitute, Chalk, Zinc oxide,	1·550	1·720	37·5	183	550
11	31	6	6 15 40 2	Brown substitute, Chalk, Zinc oxide, Paste,[1]	1·600	1·806	36	145	310
12	39	0	4 10 3 3 0·5 32 8	Brown substitute, Chalk, Zinc oxide, Metal,[1] Paraffin wax, Fluor spar, Mixture,[1]	1·650	1·920	24	81	270
13	22	0	8 52 0·5 0·5 11 6	Golden sulphide, Chalk, Paraffin wax, Paste,[1] Recovered rubber, Brown substitute,	*n.c.*	1·760	41·5	116	140
14	30	0	40 25 3 2	Chalk, Zinc oxide, Metal,[1] Paste,[1]	*n.c.*	1·903	38·5	161	125
15	30	0	18 3 2 35 12	Chalk, Metal,[1] Paste,[1] Fluor spar, Lead oxide,	*n.c.*	2·041	22·5	61	110

[1] For further information on these compounds, *see* page 174.

n.c. No change.

Physical Tests.

No.	Change of Form under the Influence of Strong Compression. Initial Thickness.	Thickness of Swelled Edges.	Thickness at Centre.	Stretch of Extreme Edges.	Change of Form under the Influence of a Succession of Blows. Initial Thickness.	Thickness of Swelled Edges.	Thickness at Centre.	Stretch of Extreme Edges.	Action of Heat.
	mm.	mm.	mm.	mm.	mm.	mm.	mm.	mm.	
1	1·36	1·62	1·29	9	1·42	2·04	1·18	2·75	Normal.
2	1·26	1·75	1·24	5·50	1·32	1·72	1·08	1·50	,,
3	1·10	1·27	1·04	7·50	1·14	1·48	1·02	4·75	Evolution of vapours on raising temperature; yellow discoloration due to substitute.
4	1·18	1·25	1·04	5·25	1·28	1·42	1·07	4·50	Develops discoloration and brittleness.
5	1·10	1·20	1·03	6·50	1·09	1·16	1·01	5	At 150° becomes soft and spongy.
6	1·25	1·32	1·16	7·25	1·29	1·36	1·10	5·25	Becomes hard and brittle.
7	1·21	1·06	0·91	7·50 (12·50)	1·24	1·01	0·90	6·25	,, ,, ,,
8	0·39	0·76	0·82	7·50 (13·25)	0·92	0·87	0·75	7	Blisters and turns hard.
9	1·12	0·82	0·87	9·25 (14)	1·15	0·86	0·82	9·24	Turns still harder than preceding sample.
10	1·29	1·35	1·20	7·75	1·29	1·64	1·12	4	At from 40 to 50° curls and breaks.
11	1·34	1·41	1·27	6·50	1·38	1·46	1·24	5·25	Curls.
12	1·25	1·21	1·04	6·50 (12·50)	1·24	1·08	1·05	7	Turns very soft.
13	1·16	1·91	1·18	6·25	1·23	1·07	1·03	9 (12)	Turns spongy, and above 130° breaks.
14	1·27	0·78	1·07	8·25 (14·50)	1·24	1·06	1·03	9·25 (12·50)	Becomes brittle.
15	1·31	0·88	0·90	8 (15·50)	1·32	1·22	1·04	8·25 (12)	Becomes spongy and brittle.

Chemical Tests.

C.—Samples of Ebonite Manufactures.						Action of H_2SO_4. Modifications in Weights per cent.	Action of $C_2H_4O_2$. Modifications per cent.	
No.	India Rubber per cent.	Sulphur per cent.	Quantity and Nature o Admixtures.		Specific Gravity.		Volumes.	Weights
XXXIII.	80	20	0	...	1·095	− 2·028	*n.c.*	+ 0·746
XXXIV.	60	20	10 10	Turpentine, . . Colophony, . .	*n.c.*	+15·183	*n.c.*	− 3·501
XXXV.	50	20	15 15	Turpentine, . . Colophony, . .	*n.c.*	− 2·018	+2·608	− 4·989
XXXVI.	60	20	20	Asphaltum, . .	*n.c.*	+28·531	*n.c.*	− 7·345
XXXVII.	40	20	40	Asphaltum, . .	*n.c.*	− 9·504	*n.c.*	− 9·127
XXXVIII.	70	20	10	Vermilion, . .	1·177	− 3·225	+2·000	− 0·114
XXXIX.	60	20	20	Vermilion, . .	1·384	+17·551	*n.c.*	*n.c.*
XL.	40	20	10 30	Turpentine, . . Slaked lime, . .	1·275	− 2·603	+3·200	+25·454
XLI.	10	20	10 60	Turpentine, . . Slaked lime, . .	1·311	− 7·880	+4·964	+61·148
XLII.	40	20	10 30	Turpentine, . . Magnesia, . .	1·203	− 4·203	*n.c.*	− 1·296
XLIII.	10	20	10 60	Turpentine, . . Magnesia, . .	1·428	− 8·333	*n.c.*	− 2·886
XLIV.	65	20	...	...	*n.c.*	*n.c.*	*n.c.*	*n.c.*

Physical Tests.

C.—Samples of Ebonite Manufactures.						Modulus of Pressure per 1² mm.	Modulus of Resistance per 1² mm.	Distensibility in mm. per 100 mm.
No.	India Rubber per cent.	Sulphur per cent.	Quantity and Nature of Admixtures.		Specific Gravity.	grms.	grms.	
XXXIII.	80	20	0	...	1·095	43·5	105	145
XXXIV.	60	20	10 15	Turpentine, . . Colophony, . .	*n.c.*	15	142	175
XXXV.	50	20	15 15	Turpentine, . . Colophony, . .	*n.c.*	12	46	135
XXXVI.	60	20	20	Asphaltum, . .	*n.c.*	17	69	145
XXXVII.	40	20	40	Asphaltum, . .	*n.c.*	24	244	175
XXXVIII.	70	20	10	Vermilion, . .	1·177	32·5	197	185
XXXIX.	60	20	20	Vermilion, . .	1·384	61	341	190
XL.	40	20	10 30	Turpentine, . . Slaked lime, . .	1·275	22·5	122	275
XLI.	10	20	10 60	Turpentine, . . Slaked lime, . .	1·311	10	55	285
XLII.	40	20	10 30	Turpentine, . . Magnesia, . .	1·203	31·7	390	105
XLIII.	10	20	10 60	Turpentine, . . Magnesia, . .	1·428	25·9	272	101·25
XLIV.	65	35	...	...	*n.c.*	excellent	excellent	incommensurable

Chemical Tests.

No.	Action of NaOH. Modifications per cent.		Action of NH_3. Modifications per cent.		Action of Colza Oil. Modifications of Volumes per cent.	Action of Mineral Oils. Modifications of Volumes per cent.	Action of Mixture of Mineral Oils, 90 per cent.; Tallow, 10 per cent. Modifications of Volumes per cent.	Action of Coal Gas. Modifications of Volumes per cent.
	Volumes.	Weights.	Volumes.	Weights.				
XXXIII.	*n.c.*	− 2·692	*n.c.*	+0·490	+12·068	+ 7·874	+20·000	+11·629
XXXIV.	*n.c.*	− 1·426	*n.c.*	+0·611	+ 2·728	*n.c.*	+ 2·982	+11·339
XXXV.	*n.c.*	− 0·187	*n.c.*	+0·428	+ 1·428	*n.c.*	+ 6·293	+ 8·053
XXXVI.	*n.c.*	− 0·112	*n.c.*	+0·344	+ 6·440	+ 1·418	+26·086	+11·804
XXXVII.	*n.c.*	− 3·192	*n.c.*	+0·488	+ 4·918	+ 1·515	+16·883	+10·062
XXXVIII.	*n.c.*	− 3·182	*n.c.*	+0·406	*n.c.*	+11·956	+41·758	+ 8·571
XXXIX.	*n.c.*	− 2·361	*n.c.*	+0·281	*n.c.*	+ 7·777	+33·707	+ 0·581
XL.	*n.c.*	− 1·404	*n.c.*	−0·689	+ 0·862	+ 0·862	+20·000	+ 9·311
XLI.	−2·054	−14·145	−1·351	−8·198	*n.c.*	*n.c.*	+ 7·284	+ 7·296
XLII.	*n.c.*	− 1·278	*n.c.*	+0·396	*n.c.*	*n.c.*	*n.c.*	+ 7·472
XLIII.	*n.c.*	− 0·539	*n.c.*	+0·396	*n.c.*	*n.c.*	*n.c.*	+ 4·510
XLIV.	*n.c.*	− 0·646	*n.c.*	*n.c.*	*n.c.*	*n.c.*	*n.c.*	+ 3·569

Physical Tests.

No.	Change of Form under the Influence of Strong Compression.				Change of Form under the Influence of a Succession of Blows.				Insulating Power. Observed Depressions.	Action of Heat.
	Initial Thickness.	Thickness of Swelled Edges.	Thickness at Centre.	Stretch of Extreme Edges.	Initial Thickness.	Thickness of Swelled Edges.	Thickness at Centre.	Stretch of Extreme Edges.		
	mm.	mm.	mm.	mm.	mm.	mm.	mm.	mm.		
XXXIII.	1·25	1·44	1·17	4·50	1·26	1·23	1·20	*n.c.*	103	Normal.
XXXIV.	2·30	1·71	*n.c.*	10·50	2·38	2·25	2·25	10·00	575	Evolution of vapour.
XXXV.	1·04	0·89	0·89	11·50	2·07	1·57	1·57	*n.c.*	8	,,
XXXVI.	1·67	1·65	1·66	11·00	1·92	1·67	1·67	11·25	60	Becomes soft.
XXXVII.	1·72	1·54	1·58	12·25	2·81	2·24	2·25	11·00	2	,,
XXXVIII.	0·96	0·86	0·87	10·00	0·98	0·87	0·87	11·25	111	Normal.
XXXIX.	0·91	0·89	0·89	10·00	0·95	0·93	0·93	10·00	46	,,
XL.	1·20	1·42	1·02	7·50	1·22	1·41	0·98	6·50	105·5	Evolves H_2S.
XLI.	1·56	1·67	1·21	3·50	1·36	broken	*n.c.*	*n.c.*	3	,,
XLII.	1·32	0·79	0·89	12·50	0·97	0·76	0·89	11·50	220	Normal.
XLIII.	0·61	0·50	0·50	11·25	0·62	0·55	0·57	11·00	218	,,
XLIV.	1·27	1·27	1·27	10·00	1·25	1·29	1·29	splintered	68	,,

n.c. No change.

The vulcanising compounds repeatedly alluded to in the foregoing tables are 'secret' preparations, the employment of which, as is evidenced by the behaviour of the samples prepared with them, generally results in the production of defective goods. PAHL and HEINZERLING have analysed these products and found their composition as follows:—

Metal.—A mixture of sulphur with the constituents of ultramarine.

Paste.—Paraffin wax, or a mixture of resin with certain organic residues: the whole dissolved in turpentine, and mixed with plaster of Paris, lime, and magnesia.

Mixture.—A solution of regenerated rubber in turpentine.

The following are the conclusions arrived at by PAHL and HEINZERLING at the end of their numerous and laborious experiments:—

1. All organic or mineral additions diminish the *elasticity* of soft rubber goods; vulcanisation with 10 per cent. of sulphur produces the best results in point of elasticity. On the other hand, certain organic substances such as turpentine, colophony, asphaltum, and likewise certain inorganic compounds such as vermilion and slaked lime, not only do not diminish the elasticity, but often even increase it.

2. The *resistance to pressure* of soft rubber goods is, to a certain degree, increased by the addition of asphaltum, chalk, fluor spar, zinc oxide, and especially by calcined magnesia. The resistance of hard rubber is increased by the addition of vermilion and of magnesia, likewise by prolonged vulcanisation and a higher proportion of sulphur. All other additions of inorganic and organic compounds, with the exception of asphaltum in small quantity, decrease the resistance.

3. Additions of mineral substance such as zinc oxide, litharge, chalk, magnesia, lime, also asphaltum and glycerine, improve the *mechanical strength* of soft rubber. Provided certain limits are not exceeded, this is also true for hard rubber containing asphaltum, turpentine, and colophony, together with chalk or magnesia. On the other hand, the mechanical resistance of india rubber is sensibly diminished by the addition of vulcanised oils (substitutes), turpentine, and paraffin wax.

4. The opinion that pure india rubber mixed with sulphur is the best *insulator* is erroneous. Mixtures of india rubber with zinc oxide, lime, magnesia in small quantities, antimony pentasulphide, brown substitute, white substitute in very small quantities, turpentine, colophony, and paraffin wax all give superior results. Especially mixtures of india rubber and paraffin wax stand out very prominently in this respect. Vermilion and litharge, on the other hand, reduce the dielectric properties of india rubber, and magnesia in large proportions has a similar effect. The worst results under all circumstances are obtained with cold cured india rubber.

5. All mixtures of india rubber with organic compounds give off vapours at temperatures from 130 to 150° C. For articles which in use are exposed to higher temperatures, such admixtures should therefore be

avoided. The other compounding materials generally behave well in this respect.

6. All mixtures containing chalk, fluor spar, litharge, and zinc oxide are strongly acted upon by sulphuric and acetic acid. The action of these acids always causes a considerable increase in weight due to the formation of either insoluble or basic salts.

The destructive action of all oils upon india rubber is more particularly checked by the addition of litharge and zinc oxide; other inorganic admixtures are much less effective. The mixtures examined in the foregoing tables are not sufficiently modified by either the alkalies or coal gas to allow any definite conclusions to be drawn. All organic admixtures protect the compound more or less from the corrosive action of the acids.

7. There is a general tendency in india rubber containing inorganic admixtures to harden and become brittle on prolonged storing. They also offer less resistance to mechanical influences, but their insulating power appears to remain unimpaired.

All those who have any practical acquaintance with the manufacture of india rubber goods will entirely agree with the above conclusions, considered merely as general statements. But while I respect the enormous amount of painstaking work accomplished in these tables by the authors, I nevertheless think it should be pointed out that the value of the tables (A) is much diminished by the fact that all the compoundings were vulcanised under identical conditions of temperature and pressure and time. But, at the same time, the ratio of sulphur to rubber varies enormously, from 10 to 100 per cent., so that practically in each test the most important of all vulcanising conditions, the ratio (sulphur : rubber), will not bear comparison with any of the other tests. Therefore the difference in the degree of vulcanisation of the different samples must have been enormous, even if we leave altogether out of account that, for the same ratio of S/R, the degree of vulcanisation in samples vulcanised under identical physical conditions varies very considerably with the nature and quantity of even such inorganic admixtures which we know to be indifferent to sulphur. For these reasons I fear that these tables do not give us any very reliable indication of the influence of the inorganic and organic admixtures experimented with upon the manufactured india rubber. This uncertainty, no doubt, affects the chemical tests to a very considerable degree, but even more so the physical tests.

As regards the tables (B), I must confess to being altogether unable to comprehend the meaning of these compoundings, the greatest part of which appear to me as extraordinary specimens of the 'rubber mixer's' fancy and imagination. Perhaps my experience of rubber manufactures is not sufficiently extensive, but, excepting the first nine specimens, I certainly must confess that I could not name any article which might be manufactured from the compoundings specified from No. 10 onwards.

CHAPTER V.

VULCANISERS AND SULPHUR CARRIERS.

THE chemical and physical aspects of the vulcanising process have been fully dealt with in the foregoing chapters, not only as regards the vulcanisation with sulphur and chloride of sulphur, but also as regards the various other processes proposed at different times, and perhaps also practised, though, no doubt, often experimentally only. The question of vulcanisers and sulphur carriers from the manufacturing point of view is, however, well worth a separate discussion, for not only are commercial brands of sulphur, chloride of sulphur, and the various recognised sulphur carriers apt to vary in composition, but also to contain impurities capable of affecting the india rubber detrimentally. A constant control of the vulcanising materials used in the factory is therefore one of the most important tasks of the rubber works' chemist.

Sulphur.—As is well known, sulphur exists in a number of modifications, which, apart from their morphological distinctions, differ from each other, in some cases considerably, in their physical properties, and show also unmistakable, if slight, differences in their chemical behaviour. We possess at present no positive information which would enable us to decide whether these differences have any effect upon the vulcanising properties of these various modifications. Since the vulcanising temperatures lie more or less considerably above the melting point of sulphur, it might, perhaps, *a priori* be assumed that no such differences in the vulcanising properties of the various modifications of sulphur can exist, but it is not at all improbable that differences of molecular aggregation and configuration of at least some of these modifications actually persist in the fused sulphur, and some little support for this proposition is perhaps to be found in the empirically established fact that the different kinds of sulphur not infrequently produce rather different vulcanisation results. This applies more particularly to the crystalline, as distinguished from the amorphous, kinds of sulphur.

The modifications of sulphur are very numerous, and the subject is by no means exhausted from the scientific point of view. We need not, however, deal here with the rare and somewhat doubtful modifications of this

element, but confine ourselves to the commonly occurring ones. These are:—

I. *Ordinary Rhombic (Octahedral) Sulphur.*—M.P. 111–114° C., B.P. 448° C., Sp. Gr. 2·060 to 2·070.

II. *Monoclinic (Prismatic) Sulphur.*—M.P. 117·4–120° C., Sp. Gr. 1·958. This modification is rather unstable, and readily reverts to the first and denser modification.

These crystalline modifications are very soluble in carbon bisulphide and in a large number of organic solvents. It is, indeed, questionable whether any organic body exists which does not dissolve sulphur. Some of the determined solubilities are:—

100 parts of	Carbon bisulphide	at	15° C.	dissolve	37	parts of S.
,, ,,	,,	,,	46	,,	73	,, ,,
,, ,,	Benzene	,,	26	,,	0·965	,, ,,
,, ,,	,,	,,	71	,,	4·377	,, ,,
,, ,,	Toluene	,,	23	,,	1·479	,, ,,
,, ,,	Ether	,,	23·5	,,	0·972	,, ,,
,, ,,	Chloroform	,,	22	,,	1·250	,, ,,
,, ,,	Phenol	,,	174	,,	16·350	,, ,,
,, ,,	Aniline	,,	130	,,	85·270	,, ,,

The solubility of sulphur in acetone I found to be as follows:—

At 10° C., . . .	0·04 per cent.
,, 22·5 . . .	0·08 ,,
,, 56 . . .	0·25 ,,

III. *Amorphous Sulphur.*—This seems to exist in a great number of varieties. Most of the amorphous varieties are insoluble in carbon bisulphide, but, according to DEVILLE,[1] these are to a considerable extent soluble in chloroform, ether, and alcohol. The conditions determining the reversion of insoluble to soluble sulphur were investigated by KÜSTER,[2] who showed that the two modifications not only differ in their molecular weights, but that they must be regarded not only as physical, but also as chemical isomers, comparable to the allotropic modifications of oxygen.

Very finely subdivided sulphur is at ordinary temperatures slowly oxidised by atmospheric oxygen. This is, no doubt, the reason why the variety known as 'flowers of sulphur' invariably contains a small amount of sulphuric acid, occasionally as much as 0·5 per cent. In this respect it is, however, remarkable that the still much more finely subdivided 'precipitated sulphur' very rarely shows any trace of acidity.

The chiefly used commercial varieties of sulphur are:—

1. **Sulphur sticks.**
2. **Flowers of sulphur.**
3. **Milk of sulphur.**
4. **Precipitated sulphur.**

[1] *Journ. prakt. Chem.*, 56, 359. [2] *Ztschr. f. anorg. Chem.*, 18, 365.

1. For the analysis of sulphur in *sticks* or *lumps*, in which form it is generally used for 'sulphur baths,' a determination of the ash present is all that is required. This is carried out by careful ignition of a few grammes of sulphur in a porcelain crucible, and weighing the residue.

Arsenic occurs only in very minute quantities in Sicilian sulphur, but not inconsiderable quantities are often to be found in 'recovered' sulphur. It may be present in the form of arsenious acid or as arsenious sulphide. The presence of these compounds is detected by treating the carefully ground sample at a temperature of 80° C. with a 10 per cent. solution of ammonia, filtering, and evaporating the filtrate. Or the filtrate is acidulated with hydrochloric acid, the arsenious sulphide which separates out filtered off and determined separately, while the arsenious acid in the filtrate is determined by the well-known methods.

Selenium, which occurs not infrequently, is of no account for the purpose of vulcanisation; moreover, it is only present, if at all, in extremely small quantities.

2. *Flowers of Sulphur* call for rather more careful analysis. The ash is determined as above described. The acidity is ascertained by suspending 5 to 6 grms. of the powder in from 80 to 100 c.c. of water and titrating with a $\frac{1}{10}$ standard solution of caustic soda. As the 'flowers' are only with great difficulty wetted by the water, it is to be recommended to weigh the quantity to be used for titration in a dry wide-necked flask, and moisten the sulphur with a small quantity of alcohol. If now the water is added, a good suspension is readily obtained. The total acidity ascertained is calculated as sulphuric acid. How much acid is admissible must, of course, somewhat depend upon the quality of the products for the vulcanisation of which the sulphur is to be employed; but considering how greatly even a very small amount of sulphuric acid may affect the resiliency of india rubber articles, not more than 0·2 per cent. should ever be allowed, and for all those goods in which either high elasticity or lightness of colour are important considerations, sulphur containing acid should be altogether avoided.

In many cases flowers of sulphur contain a somewhat large amount of moisture. This should be determined by drying in a desiccator at ordinary temperature. Drying in a stove, owing to the not inconsiderable vapour tension of sulphur at 100° C., is apt to give entirely erroneous figures.

I consider it further desirable to determine the proportions of soluble and of insoluble sulphur by treating for an hour 5 grms. of the sample with 50 c.c. of carbon bisulphide, shaking the mixture at frequent intervals. The solution is separated from the insoluble portion by filtration, and the filter residue washed with a small volume of carbon bisulphide. The filtrate and washings are collected in a weighed flask. After distilling off the bisulphide and drying the flask while still hot by a moderate air blast, the amount of soluble sulphur is ascertained by weighing. The insoluble portion, of course, represents insoluble sulphur, ash, acids, and moisture.

It is surprising how tenaciously rubber manufacturers cling to the use of flowers of sulphur for vulcanising purposes, considering that this product is one of the most variable and impure forms of commercial sulphur.

3. *Milk of Sulphur.*—Under this name a product is offered which is supposed to offer advantages over flowers of sulphur. All the samples I have met with contain a more or less considerable amount—20 to 30 per cent.—of calcium sulphate. Very often this product contains also soluble salts, in which case it is invariably strongly hygroscopic. As often as not, free acid is present. Altogether, there is nothing in this preparation to recommend it to the rubber manufacturer.

4. *Precipitated Sulphur.*—This, undoubtedly the best of all forms of sulphur for vulcanising purposes, is prepared by the precipitation of sulphur from the solutions of polysulphides with hydrochloric acid under closely defined conditions. It forms an impalpable powder presenting, under the microscope, the appearance of very small globules of amorphous sulphur (*see* fig. 11), but is completely soluble in carbon bisulphide. It should not contain more than 3 per cent. of moisture, nor more than a trace of ash. Neither should it contain any matter soluble in either water, dilute hydrochloric acid, or dilute ammonia.

Pahl and Heinzerling (*see* page 174) describe, under the names of 'Paste, Metal, and Mixture,' certain vulcanising compounds which are more or less complicated mixtures of quite a variety of heterogeneous substances. These preparations are at best utterly worthless; the prices at which they are sold bear no relation to their intrinsic value, and, unfortunately, their continued existence is an undeniable proof that the india rubber industry still harbours and encourages the technical superstitions of the dark ages.

Chloride of Sulphur.—This product, sulphur monochloride S_2Cl_2, is extensively employed for the process of vulcanisation in the cold. The closer the composition of the commercial product corresponds to the theoretical figures calculated for S_2Cl_2—Cl, 52·51 per cent.; S, 47·48—the better. Commercial sulphur monochloride may contain either free sulphur, of which it is an excellent solvent, or an excess of chlorine in the form of the dichloride SCl_2. Both impurities are known to occur not uncommonly. While free sulphur, however, only becomes objectionable if its amount exceeds certain limits, the presence of sulphur dichloride, in however small a quantity, should not be tolerated. Excess of sulphur may cause an efflorescence, technically termed 'sulphuring up,' of sulphur upon the vulcanised surfaces, which, although objectionable from the point of view of appearance, does not affect the soundness of the vulcanisation; but the presence of comparatively small quantities of the dichloride produces a disagreeable and more or less pronounced hardness in the india rubber. The cause of this is, of course, perfectly obvious and lies in the excessive chlorination of the india rubber.

The commercial article is by no means very constant in its composition and properties, and the products of different makers differ widely. Considering what was said above respecting the presence of either sulphur or chlorine in sulphur monochloride, and further, bearing in mind the serious difficulties which are likely to arise through unnoticed variations of the chloride of sulphur used for either the vulcanisation of india rubber or for the manufacture of white india rubber substitutes, the urgent necessity for the continuous analytical control of the chloride of sulphur used in a rubber factory is very obvious. It may safely be asserted that the mistrust with which the cold vulcanising process is frequently regarded is in a large measure due to the indiscriminate use of chloride of sulphur of varying composition.

Sulphur monochloride in the pure state forms a reddish-yellow liquid. Its specific gravity at 16·7° C. is 1·685 according to KOPP, 1·6826 according to FAWSITT. There appears to be some uncertainty about the boiling point, the temperatures stated by various authors ranging from 136 to 139° C.

The colour of the commercial sulphur monochloride varies[1] from a bright amber to an almost ruby-coloured liquid, but none of these varieties possesses a constant boiling point. The following are the boiling points of two typical specimens of the commercial product, which are respectively described as 'yellow product' and 'red product':—

100 c.c. yield	Yellow Product.	Red Product.
5 c.c. at	131° C.	128° C.
10 ,,	132	129
20 ,,	133	136
60 ,,	135	135
70 ,,	135	135
80 ,,	135·5	135·5
85 ,,	135·5	135·5
90 ,,	135·5	136
95 ,,	135·5	136

On analysis these two products were found to be composed as follows :—

	Yellow Product.	Red Product.	S_2Cl_2 (calcul.)
Sulphur, . . .	49·39 per cent.	46·02 per cent.	47·41 per cent.
Chlorine, . . .	50·60 ,,	53·97 ,,	52·52 ,,

These data show that an even slight excess of chlorine causes a considerable depression in the boiling points of the lower fractions. But it will also be observed that even the 'yellow product,' containing a slight excess of sulphur, possesses a range of boiling points extending not inconsiderably below the true boiling point of sulphur monochloride. The cause of this is by no means certain, but probably finds its explanation in

[1] It will be clearly understood that the boiling of S_2Cl_2 is perfectly constant—*i.e.*, not accompanied by any decomposition. HÖHN's contradicting statement (*Gummi Zeitung* [14], 1899, p. 34) is entirely erroneous. The irregularity of the boiling point of the commercial article is, of course, due to its impurity.

the law of partial vapour tensions as exhibited by solutions of two volatile bodies—S_2Cl_2 and S.

It is scarcely ever necessary to make a complete analysis of sulphur chloride. For practical purposes it is sufficient to determine the quantity of one of its constituents, and determine the amount of the other by the difference. This calculation is carried out by estimating the amount of chloride of sulphur corresponding to the estimated percentage of that constituent, the amount of which falls short of the theoretical figure. The amount of chloride of sulphur thus ascertained is deducted from 99·99, and the difference then shows the absolute excess of the constituent over the theoretical figure. Thus we find, on comparison of the analytical figures of the yellow product, as above quoted, with the theoretical figures given, that it contains less than the theoretical amount of chlorine—50·60 instead of 52·52 per cent. But 50·60 per cent. of chlorine represents 96·34 per cent. of chloride of sulphur S_2Cl_2, and deducting the latter amount from 99·99, we obtain the absolute excess of free sulphur present as 3·65 per cent. In exactly analogous manner the absolute excess of free chlorine present in the above quoted 'red product' is ascertained as 3·05 per cent.

The analysis of chloride of sulphur is, according to Fawsitt,[1] carried out in the following manner:—

1. *Sulphur.*—Small, weighted, thin-walled glass bulbs are filled with the chloride of sulphur; the points are then sealed in a gas flame for the purpose of weighing. After ascertaining the weight of the chloride of sulphur, the point is broken off, and the bulb immersed in 25 c.c. of concentrated nitric acid in a small flask. If necessary, the rate at which the reaction proceeds is moderated by cooling the flask. If sulphur separates out, this is oxidised by the addition of potassium chlorate. Oxidation being completed, the contents of the flask are emptied into an evaporating dish, the flask washed with warm water, the washings added to the acid in the dish, and the whole evaporated until all the nitric acid has disappeared. This operation may be hastened by the addition of hydrochloric acid. The residue is finally dissolved in water, and the amount of sulphuric acid formed determined by weighing as barium sulphate.

2. *Chlorine.*—One of the bulbs containing a weighed quantity of chloride of sulphur is allowed to drop into a 250 c.c. glass-stoppered flask containing water or weak caustic soda solution. The contents of the flask are repeatedly and violently shaken. The decomposition being completed, the flask is filled up to the mark with water. An aliquot part of the solution is then taken, neutralised with caustic soda, boiled for a few minutes, and subsequently acidulated with nitric acid. Any sulphur separating out is filtered off, and the hydrochloric acid present in the filtrate determined in the well-known manner.

Of these two processes the first gives very satisfactory results, but the operation is by no means a pleasant one. It becomes rather troublesome if

[1] *Journ. Soc. Chem. Ind.*, 1886, p. 638.

sulphur, the oxidation of which is sometimes very tedious, separates out. The method for the determination of the chlorine is very unsatisfactory. Should the small bulb fail to break on shaking the flask, the completion of the decomposition may require days. The process is very slow under all circumstances, and cannot safely be accelerated by heating. Of course, as I have shown above, it is quite sufficient to determine only the percentage of sulphur contained in the chloride of sulphur, and to calculate from this figure the chlorine. In this case FAWSITT's above described method may be used.

I prefer, however, the determination of the chlorine by the following method as a quicker and even more accurate process:—Place in a weighed 200 c.c. flask (glass-stoppered) about 10 c.c. of the chloride of sulphur to be examined, and ascertain the weight of this volume; then fill up to the graduation mark with pure benzene. Of this solution run 5 c.c. into 20 c.c. of a solution of sodium ethylate contained in a wide-necked flask of about 150 c.c. capacity. The solution of sodium ethylate contains 5 grms. of metallic sodium in 100 c.c. of absolute alcohol. The mixture is then very gently shaken, allowed to stand for an hour on the water bath, evaporated to dryness, and subsequently heated for one hour in a water oven. The contents of the flask are then dissolved in about 75 c.c. of boiling water faintly acidulated with nitric acid, 10 c.c. of a 10 per cent. solution of cupric sulphate added, the whole heated for a few minutes on the water bath, filtrated, and the filter residue washed with hot water. In the filtrate the chlorine is then determined as silver chloride. The results obtained by this method are very accurate.

The treatments of rubber with either sulphur or chloride of sulphur are the only methods at present employed for vulcanisation. It is true other methods have been suggested and often also practically tested, but none have gained a foothold in manufacturing. GÉRARD's process of treating the india rubber for three hours in a solution of calcium pentasulphide (1·205 sp. gr.) under a pressure of 60 pounds (140° C.) yields very satisfactory results, but the method offers no advantage over the ordinary processes. It is, nevertheless, worth remembering that the principle involved in this process—vulcanisation with molecular sulphur in a nascent state—would, if a substance could be found by means of which it could be employed successfully, lead to very considerable and highly desirable improvements of the vulcanising process (*cf.* page 106). FAWSITT's process[1] is not so much a *new vulcanising process*, as one based upon the employment of a new sulphur carrier, antimony iodide. For a variety of reasons also, this process proved not more than a partial success, and though much was expected of it, it never came into general use. My own process[2] is a much simpler application of the same principle, and is also rather cheaper. It allows the shortening of the time of vulcanisation by almost one half, or else a reduction in the same proportion of the amount

[1] Eng. Pat., No. 17,197, 1890. [2] *Ibid.*, No. 16,937, 1900.

of sulphur employed. Either of these alternatives represents a very important advantage, consisting either of a substantial saving of time—*i.e.*, increased power of production—or in a very large reduction of the amount of free sulphur contained in the india rubber, thus entirely preventing the objectionable appearance of the rubber 'blooming' or 'sulphuring up.' It is, however, impossible at the present moment to say whether the process will bear the test of time.

Lead Thiosulphate and other Lead Compounds.—Various preparations of lead thiosulphate occur in commerce under the trade designation of 'Hypo' and 'Black Hypo.' A compound may be manufactured in the wet way by precipitating a solution of lead nitrate with an equivalent quantity of sodium thiosulphate. The product, if carefully prepared, forms an almost white, micro-crystalline powder; or a plumbago-coloured product may be obtained by heating a mixture of white lead and sulphur. The first of these two preparations is technically pure lead thiosulphate (PbS_2O_3); the second contains varying amounts of this salt, lead sulphate, lead sulphide, and considerable quantities of unaltered white lead. To the lead sulphide it owes, of course, its greyish-black colour.

'Hypo' is frequently advertised as an infallible agent for the prevention of 'sulphuring up' of rubber goods, and as a vulcaniser, the use of which does away with any risk of overcuring. Both statements are more or less obvious exaggerations, and probably every experienced rubber manufacturer has seen goods produced with 'Hypo' damaged by 'sulphuring up' or by overvulcanisation, or by both.

The truth is that 'Hypo,' like all lead compounds, acts as a sulphur carrier, and thus facilitates the vulcanisation; and there is also no doubt that the presence of lead sulphide has a restraining influence upon the further addition of sulphur to rubber as soon as a certain degree of vulcanisation has been reached. In this sense 'Hypo,' or, rather, the lead sulphide into which it is converted during vulcanisation, has the property, within certain limiting conditions, of reducing the risk of overvulcanisation. From experiments I have made, it appears, moreover, that 'Hypo,' or, at least, that part of it which may be described as lead thiosulphate, is by itself capable of producing vulcanisation. A series of experiments which I made leave no doubt on this point, and the explanation of this fact is probably to be found in the circumstance that one of the decomposition products of lead thiosulphate under the influence of high temperature is sulphur:

$$4PbS_2O_3 = PbS + 3PbSO_4 + 2S_2.$$

Lead thiosulphate is, therefore, more properly described as a vulcaniser than as a sulphur carrier, but in the exertion of its vulcanising properties it forms at the same time, according to its above suggested decomposition, two sulphur carriers—lead sulphide and lead sulphate. Of these, as might be expected, lead sulphide is much the more active.

The most generally used sulphur carrier is, however, neither lead

thiosulphate nor lead sulphide, but lead oxide, commonly known as litharge.

While there is no doubt respecting the accelerating effect of these lead compounds upon the rate and the amount of the sulphur addition in the vulcanising process, the nature of this action is very little understood. It is generally assumed that in the first instance lead sulphide is formed, and that this exerts the above named accelerating effect by the intermediate formation of unstable polysulphides. But even taking this view as correct, this assumption cannot be said to be an explanation. Indeed, the very difficulty of an explanation of this 'catalytic' action lies in the fact that the energy transformation due to a certain reaction remains absolutely the same, however many intermediate phases or reactions we interpolate between the limiting terms of the reacting system.

To the rubber manufacturer these sulphur carriers are of very considerable importance, their use enabling him to increase the degree of vulcanisation within considerable limits without recourse to either an objectionable excess of sulphur, undesirably high temperatures, or very undue prolongation of the vulcanising process. The beneficial effect of these sulphur carriers in these respects is so marked that at the present time the majority of rubber goods in which a white or drab colour is not essential contain more or less of one of the above named substances. Litharge especially is very freely used for this purpose.

Whether litharge acts in the india rubber as a sulphur carrier only is by no means certain. That it may act also in other ways is to be inferred from the observation, which is quite familiar to most india rubber workers, that mixtures of india rubber with a large proportion of litharge are apt to become very hot during their treatment between the mixing rollers. In extreme cases the mixture, in spite of its high temperature, grows continually harder, until eventually it forms a mass of crumbs or flakes possessing little cohesion and adhesiveness, and which can no longer be rolled into a sheet. The cause of this behaviour is unknown, but will probably be found in the incontestible fact that india rubber absorbs a not inconsiderable amount of oxygen while it is being worked upon the mixing rollers. This oxidation process is intensified and accelerated by the litharge present, which is known to act as an oxygen carrier. Certain it is that none of the other lead compounds[1] used in conjunction with india rubber exhibit this action in the slightest degree.

A complete analysis of the above named lead compounds may, of course, under certain circumstances become necessary, but is not necessary for ordinary purposes. The following tests will usually suffice :—

Lead Thiosulphate.—Composition PbS_2O_3, containing 64·89 per cent. of lead. Commercial samples should not contain less than 60 per cent. of Pb. This is ascertained by boiling about 1 grm. of the sample with dilute

[1] Not even white lead, which, according to its approximate formula $(PbCO_3)_2 Pb(OH)_2$, contains about 81 per cent. of lead hydroxide.

nitric acid (10 per cent. HNO_3) until the precipitate is perfectly white, and the supernatant liquor free from lead. The precipitate is then filtered, washed neutral, dried, removed from the filter, placed in a crucible for about fifteen minutes heated to a temperature not exceeding 130° C., and subsequently weighed. The yield of $PbSO_4$ thus obtained should not be less than 88 per cent. Lead thiosulphate should be almost completely soluble in a 20 per cent. solution of sodium thiosulphate at a temperature not exceeding 50° C.

Black Hypo.—This product is extremely variable in its composition, representing generally a mixture of lead carbonate, sulphide, thiosulphate, sulphate, and free sulphur. Occasionally the product bearing this name is simply a mixture of lead sulphide with sulphur. For the purpose of analytical control, a determination of the total lead and of the free sulphur present is sufficient, but what there should be in amount it is impossible to say. The analyses will therefore have to be made in reference to an adopted standard.

Litharge, PbO.—If it is thought desirable, the total lead present may be determined by dissolving a weighed quantity in nitric acid, with addition of a crystal of oxalic acid, precipitating the filtered solution with sulphuric acid, and weighing the lead sulphate precipitated. Litharge should always be tested for the absence of lead peroxide and copper. Dissolve a small quantity of the sample in as little nitric acid as possible. A dark, blackish-brown residue dissolving after the addition of a small crystal of oxalic acid indicates the presence of lead peroxide. The solution obtained is now treated with sulphuric acid in slight excess, the lead sulphate precipitated is filtered off, and an excess of ammonia added to the filtrate, when the presence of copper is shown by the appearance of the well-known blue coloration.

Red Lead is frequently used in small quantities in rubber mixings, with a view to 'harden' the rubber. I do not consider this as a satisfactory addition, as this hardening effect is obviously due to a partial oxidation of the india rubber, which appears to me to be a particularly undesirable manner of obtaining such an effect, which can, moreover, be produced by a variety of other means in quite an unobjectionable manner.

Antimony Pentasulphide.—Antimony pentasulphide, Sb_2S_5, commercially known as 'Golden Sulphide,' is the most important and the most efficient sulphur carrier used in conjunction with india rubber. It is looked upon by many, not only as a sulphur carrier, but as a vulcaniser itself. This view is, however, based upon undoubtedly erroneous observations. The pure pentasulphide is quite incapable of effecting the vulcanisation of india rubber. Commercial pentasulphides will indeed vulcanise india rubber without special addition of sulphur, but this is simply due to the fact that they all contain free sulphur in quantities ranging from 5 to as much as 30 per cent. This free sulphur, at any rate as far as the lower percentages are concerned, cannot be looked upon as a mere

adulteration, for, without entering into any details of its manufacture with which in this place we are not concerned, there is no doubt that the amount of free sulphur in a given sample of pentasulphide plays a determining part in the production of a pentasulphide of a certain colour.

The colour of golden sulphide varies from a full orange-tan colour to almost a purplish-scarlet, German rubber manufacturers preferring the former, their French colleagues the latter variety, whilst in English factories an intermediate shade is almost exclusively used.

The properties of antimony pentasulphide are rather interesting. Heated to the boiling point of sulphur, 448° C., with exclusion of the air, it decomposes into antimony trisulphide, Sb_2S_3, and sulphur. Treatment with hydrochloric acid in the cold produces exactly the same decomposition. Ammonia dissolves it on gentle heating, any antimonious acid, Sb_2O_3, and free sulphur present remaining undissolved. The behaviour of different samples of pentasulphide with boiling carbon bisulphide varies very considerably, in some cases reduction to Sb_2S_3 taking place. Equally marked is the behaviour of different samples on drying them at 110° C.

Considering the fact that even in products of the same colour the percentage of free sulphur present may exhibit considerable variations, it is evident that, apart from the question of colour, all samples and deliveries of antimony pentasulphide should invariably be analysed. The neglect of this precaution is likely to cause most objectionable variations and difficulties in the vulcanising process.

The most obvious method for the determination of the amount of free sulphur present—by the extraction of a weighed quantity of the sample with bisulphide of carbon—cannot be employed in this case, owing to the more or less pronounced decomposing action of this solvent upon the pentasulphide. Short of the rather tedious complete analysis, the most satisfactory test consists in treating a weighed quantity of the sulphide with strong ammonia, and heating very gently on the water bath. The pentasulphide rapidly dissolves any antimonious acid, the sulphur present remaining behind. The solution is filtered, the filter residue washed with cold dilute ammonia until the washings, on acidulation, no longer yield a deposit of pentasulphide. The filter and its contents are dried at 60° C. and treated with carbon bisulphide in a Soxhlet extractor, the extract being collected in a weighed flask. The residue remaining on the filter after extraction is antimonious acid, which is removed from the filter, dried, and weighed. Of course any adulterants would likewise remain undissolved on the filter, but it is very rarely that such adulterants occur.

Zinc Sulphide and Lithopone.—Zinc sulphide is an excellent material to compound with india rubber, but its high price on the one hand, and its yellowish colour on the other hand, restrict its use very considerably. It is, however, very largely used in the form of the brilliantly white pigment known as 'Lithopone.' This product is formed by the simultaneous pre-

cipitation of barium sulphate and zinc sulphate by the interaction of barium sulphide and zinc sulphate:

$$Ba(SH)_2 + ZnSO_4 = BaSO_4 + ZnS + H_2S.$$

Accordingly, lithopone should contain at least 29 per cent. of zinc sulphide, and no product containing less should be accepted, as this would involve a decrease both in covering power and efficiency in the vulcanising process.

Lithopone is by far and away the best material to use in 'drab' rubber goods which are subjected to the action of alkalies, but should be rigorously excluded from all goods subjected to the influence of acid solutions.

CHAPTER VI.

INDIA RUBBER SOLVENTS.

THE importance of solvents for india rubber in manufacturing has been well put forward by HANCOCK[1] himself, who notes that "it is a singular fact that, although this substance had attracted the notice of chemists from the earliest date of its importation into Europe, and some of the ablest had employed themselves upon it, they failed to discover any means of manufacturing it into solid masses or to facilitate its solution. I was at first imbued with the notion that, to make it useful, I must find a good solvent; and I think my first experiments were directed to some attempts to dissolve it in oil of turpentine, but I found I could only make very thin solutions, and these dried so badly, or, rather, not at all, that they were useless. The oil of turpentine then procurable was no doubt of inferior quality; when pure, it dries perfectly. This was about the year 1819."

As the result of this failure to discover a satisfactory solvent for india rubber, which would have enabled HANCOCK to utilise the rubber scraps which were fast accumulating at his works, he attempted to find a mechanical treatment to attain this end, and already, a year later, in 1820, he accomplished this important task by the construction of his 'masticator.' It was, however, not until two years later that he discovered that this masticated rubber dissolved with the greatest facility in 'good oil of turpentine.'

These earliest experiences show already very clearly the fact that the solubility of india rubber depends as much upon its physical condition as upon the nature of the solvent. It may, indeed, be stated that a homogeneous rubber solution cannot be produced without either first changing the physical condition of the india rubber by mechanical working, or by mechanically working the gelatinous magma produced by the treatment of unmasticated india rubber with solvents; and to obtain the best results, it is necessary to work the india rubber mechanically prior to its immer-

[1] *Personal Narrative of the Origin and Progress of the Caoutchouc or India Rubber Manufacture in England.* By Thomas Hancock, of the firm of Charles Macintosh & Co., London and Manchester. London: Longman, Brown, Green, Longmans, & Roberts, 1857 (p. 2).

sion in solvents, and to subject this crude solution to a further process in machines constructed upon the familiar principle of the paint-grinding mill. The necessity for these mechanical operations lies, of course, in the fact that all varieties of india rubber appear to contain, besides the soluble india rubber, a further product (*see* page 8), which, although insoluble, swells to enormous dimensions in the rubber solvents. As long as this substance is present in the form of particles of appreciable size, the 'rubber solution' will appear lumpy or thready, and the effect of the mechanical working consists simply in reducing these insoluble masses to particles of imperceptible size. This is done far more effectively by the mastication of the rubber than could be accomplished by the working of it after solution. It will be observed that this insoluble compound behaves in this respect much as the 'fatty substitutes,' which cannot be satisfactorily introduced into a rubber solution or dough after the rubber has once been dissolved, but have to be reduced to imperceptibly small particles by being 'dry mixed' into the rubber in a roller mill. At the same time, there can, however, be no doubt that the trituration of the insoluble constituent is not the only effect of the mastication of india rubber. The india rubber hydrocarbon itself undergoes some peculiar modification in this process which certainly renders it easier soluble, and which is also capable of profoundly altering its behaviour in the process of vulcanisation. Nothing is known respecting the cause of this remarkable phenomenon, and equally striking is the fact that the rubber films resulting from the evaporation of the solvents from coatings spread with solutions of india rubber in different solvents exhibit striking differences in their chemical properties. This applies even to solvents which may be considered to be closely related chemically to each other, such as the various terms of the hydrocarbons of the aromatic and aliphatic series respectively. In practice, this would mean that we cannot indiscriminately substitute one solvent for another, and leave the other manufacturing operations out of consideration, without some change in the state and properties of the manufactured products. This is a point which at the present time is very little appreciated.

1. **Coal Tar Naphtha.**—This is by far and away the most generally used india rubber solvent, and it is unquestionably also the best. Its composition is subject to very great variations, which chiefly depend upon the demand for benzene and toluene on the part of the coal tar colour industry, and as far as benzene is concerned, also on the demand of that article by gas works. It goes without saying that the price of the 'solvent naphtha' also closely follows the benzene market—indeed, this extends even to the prices of petroleum spirit and Scotch shale naphtha. It is therefore obvious that not only will the price of coal tar naphtha, but also its composition, vary considerably according to the demand for various specific fractions of the coal tar hydrocarbons.[1] Not infrequently are the varia-

[1] The effect of the excessively low prices, which, during the greater part of the last two years, were quoted for benzol, furnish an instructive example of this. At the time

tions due to higher prices to the advantage of the rubber manufacturer, those due to lower prices being to his detriment. In either case it is desirable, in the interest of uniform production, to test the boiling points of solvent naphtha deliveries.

Of the aromatic hydrocarbons occurring in coal tar, of course, a limited number only can, or should be, present in a good solvent naphtha, which should not contain more than 5 volumes per cent. of substances boiling above 150 or 160° C.—preferably the lower limit. Of aromatic hydrocarbons, only the following can therefore occur:—

		Boiling Point.
Benzene,	C_6H_6,	81° C.
Toluene,	C_7H_8,	111
Orthoxylene,	C_8H_{10},	141
Metaxylene,	C_8H_{10},	140
Paraxylene,	C_8H_{10},	138
Styrene,	C_8H_8,	146
Mesitylene,	C_9H_{12},	163
Pseudocumene,	C_9H_{12},	166

It is, of course, also possible for aliphatic and olefinic hydrocarbons to be present in solvent naphtha, but their quantity will always be very small. The customary methods of refining solvent naphtha, if properly carried out, would, at any rate, tend to completely eliminate the olefinic hydrocarbons.

The above named series of aromatic hydrocarbons represents a range of boiling points from 81 to 166° C., and this would fairly correspond to a solvent, 95 per cent. of which boils at 160° C., some part of the higher boiling fraction being carried over at temperatures at and below 160° C. in the ratio of their vapour tensions at these temperatures. The evaporation of benzene and toluene at ordinary temperatures is, however, so considerable that the presence of large volumes of these hydrocarbons in the solvent naphtha would cause considerable inconvenience and loss at the early stages of manufacturing, and for this reason good solvent naphtha should contain no benzene and only very little toluene. In short, the initial boiling point of solvent naphtha should, in my opinion, be not lower than 110° C., and it is highly desirable that 95 per cent. of such a naphtha should distil only a few degrees above 150° C.—the fewer, the better. Accordingly, the range of boiling points of a good naphtha should not appreciably exceed 40° C. It will be found that a solvent of this description answers admirably for the most important purposes of the rubber manufacturer. For the production of a few specialities, such as quick drying 'solution' or 'varnish,' it is scarcely volatile enough. Nor should it for this purpose be mixed with benzene, as is often done under the mistaken impression that this renders

benzol was 7d. per gallon, 'solvent naphtha' had fallen to 11d., and it was therefore greatly to the interest of the distiller, though not of the rubber manufacturer, to send out in the solvent as much benzol as possible. The result of this was that solvents which formerly used to show an initial boiling point of 107° C., now began to boil at 85° C., or lower.

the solvent quick drying, but, as a matter of fact, only renders the drying of the solution more erratic. The only satisfactory procedure is in this case to employ a differently constituted solvent—say, one boiling from 110 to 140° C. In other words, if for some purpose or other we require a 'lighter' solvent, the usually adopted method for procuring it by mixing it with fractions reducing only the initial boiling point of the original solvent is, at best, only a rather inefficient make-shift. To 'lighten' a solvent, its terminal boiling point should be lowered by keeping out the fractions of highest boiling point. The constriction of the range of boiling points thus effected may then be compensated by the addition of fractions of a lower boiling point.

The use of almost pure benzene as a rubber solvent for manufacturing purposes has sometimes been suggested, but apart from the fact that its boiling point is altogether too low, and its volatility far too high, for most practical purposes, the use of a homogeneous solvent possessing almost a constant boiling point results in solutions or 'doughs' drying from the surface and yielding harsh and rough coatings. Waterproof cloth produced with such solvents often exhibits the very objectionable defect of curling—*i.e.*, the cloth curls towards the proofing surface. The cause of this phenomenon lies in too 'light' a solvent being employed. The coating of india rubber dough on the cloth dries from the surface, the latter therefore hardening and contracting, while the lower strata, still containing the solvent, cannot contract proportionately. This differentiation in the stresses of the different strata of the rubber coating becomes permanently established if the goods are cold cured, and the inevitable result is a curling or cockling waterproof cloth. This is the simple explanation of a defect which has numberless times caused great annoyance and loss to manufacturers, and the occurrence of which is generally looked upon as a great mystery.

The specific gravity of solvent naphtha is, on the whole, a rather immaterial point bearing little or no relation to its boiling point. Beside the latter, it is of no importance whatever, unless, indeed, the solvent be bought by weight, which is very unusual. As a knowledge of the specific gravity of a solvent gives no tangible information respecting its quality, this constant calls for no special observations.

The usual method observed in rubber factories for ascertaining the boiling point of a given sample of solvent naphtha consists in distilling 100 c.c. in a fractionating flask over a naked flame at the rate of two drops per second. The distillate is collected in a graduated cylinder (100 c.c.), and the successive temperatures, and the length of time during which each fraction distils over, are noted. The following table contains a number of such tests selected from many hundreds of records. There is, however, a second method, which, as a commercial test, is much used. In this method a tubulated retort of about 250 c.c. capacity is used charged with 100 c.c. of the naphtha, and a thermometer is so fixed in the tubulus that its bulb is

exactly within three-eighths of an inch from the bottom of the retort. Accordingly, the thermometer is immersed in the liquid, and the temperature noted at which the first drop of the distillate passes over into the receiver. The first method is certainly preferable from the rubber manufacturer's point of view. The second method is altogether antiquated; it is open to a number of grave objections, although the English benzol trade adheres to it with its characteristic conservatism.

The most satisfactory method for ascertaining the boiling point of coal tar naphtha is one which was first proposed by BANNOW in 1886, and which has been very generally adopted. The apparatus used consists of the following parts:—

1. An almost spherical flask of 150 c.c. capacity made of copper 0·6 to 0·7 mm. in thickness. Its diameter amounts to about 66 mm. The form and dimensions of the neck are clearly shown by the accompanying fig. 16.

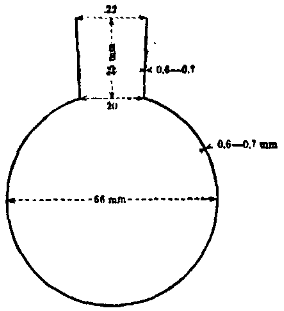

FIG. 16.—Diagram of distilling flask for benzene (naphtha) test.

2. A dephlegmator made of glass, and consisting essentially of a glass tube of about 14 mm. diameter and 150 mm. in length, the middle part of which is expanded into a bulb of moderate size. Near its upper end this tube carries a side tube of about 8 mm. diameter, the two joining at nearly a right angle, as shown in fig. 17.

The distilling flask is mounted on a draught-proof stand, the construction of which is clearly indicated in the diagram. The top of this stand is formed by a stout asbestos board in which a circular central opening 50 mm. in diameter is provided. This distilling apparatus is joined to a condenser 80 cm. in length, and so inclined that the difference of level between its two ends is 10 cm.

The flask is filled with 100 c.c. of the naphtha, and the distillation is so conducted that about 5 c.c. of distillate are obtained per minute, or approximately two drops per second. Distillation is continued until 95 c.c. have passed over, the distillate being collected in a graduated 100 c.c. cylinder.

The thermometer used should be made of thin glass, and its diameter should not exceed 7 mm., although it may be less. The bulb of the thermometer should occupy the centre of the bulb of the dephlegmator.

By means of this apparatus the boiling points of a number of rubber solvents recorded on the following page were obtained.

Of these samples, No. 1 is a little too high in boiling point, but otherwise satisfactory. No. 2 is, however, distinctly preferable. Nos. 3, 4, 6, and 7 refer to tests of a special brand of solvent naphtha, which is extensively used for waterproofing purposes. No. 3 is a thoroughly good type of this solvent, but, of course, there is, in employing it, a rather considerable loss amounting, on the average, to about 10 per cent. before it reaches the spreading machine. With the solvents 1 and 2 this loss is very slight indeed. No. 4 shows what the solvent No. 3 degenerated into at the time benzol had reached an unprecedentedly low price. The test shows that at least 50 per cent. of the solvent, and probably a good deal more, consisted simply of benzol. Seeing that, at the same time, the price of this 'special

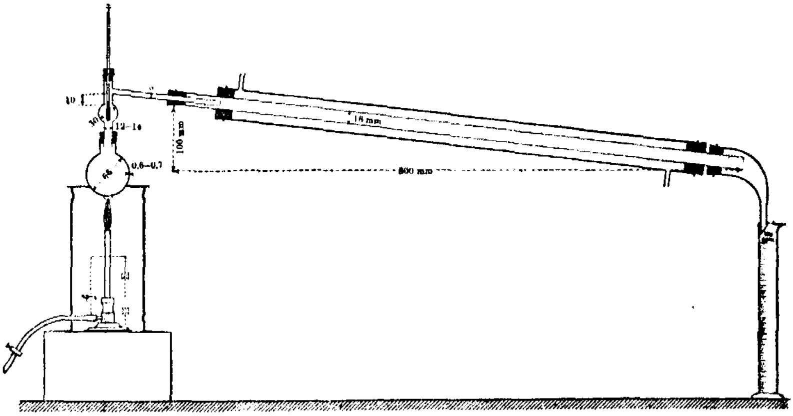

FIG. 17.—Diagram of distillation apparatus for benzene (naphtha) test.

solvent' was more than twice that of the benzol, it is evident that this adulteration was highly profitable to the maker, and proportionately detrimental to the user. No. 6 has throughout rather too low a boiling point, and this applies even more to No. 7, the range of boiling points of which is far too short, and much too low at the higher end.

A solvent naphtha furnishing a satisfactory boiling point test cannot, however, for that reason at once be passed as meeting all the requirements of the rubber manufacturer. Such a solvent may yet contain a number of impurities, the presence of which might not, and, indeed, in the majority of cases would not, appreciably affect its boiling point, but would, nevertheless, greatly prejudice its adoption.

The most important impurities are:—carbon bisulphide, naphthalene, pyridine and its homologues. Adulteration of solvent naphtha occurs very rarely, and the only possible adulterant is petroleum spirit.

The detection of carbon bisulphide may be carried out by means of the thate test. For this purpose 100 c.c. of the naphtha are distilled, and

Description of Solvent.	5° C.	10° C.	20° C.	60° C.	70° C.	80° C.	90° C.	95° C.
1. Solvent Naphtha,	121° C.	123° C.	125° C.	140° C.	146°·5 C.	153°·5 C.	158° C.	163°·5 C.
2. ,, ,,	121 ·5	124 ·5	127 ·5	139 ·5	144	151	154 ·5	158 ·5
3. Special ,,	105	107	109	119 ·5	123	127 ·5	130	133 ·5
4. ,, ,,	82	87	94 ·5	121	128	137	142	146
5. 90 per cent. Benzol,	82	83	83	86	87 ·5	91 ·5	96	106
6. Special Naphtha,	101 ·5	103	105	114	116 ·5	121 ·5	123	126
7. ,, ,,	103 ·5	105	108	112	113	114 ·5	115 ·5	117
8. Petroleum Spirit,	58	68	76	98	122	131	146	157
9. ,, ,,	34	51	71	94	118	129	146	158
10. ,, ,,	31	50	71	96	119	129	144	161
11. ,, ,,	42	54	75	98	120	132	148	161
12. ,, ,,	40	54	73	93	119	131	147	159
13. ,, ,, fractionated,	30	84	91	119	125	129	133	141
14. ,, ,, ,,	79	81	87	113	120	127	135	142
15. Shale Spirit,	80	93	100	120	128	135 ·5	143	151 ·5
16. ,, ,,	78	87	96 ·5	118	127	134	145	154
17. ,, ,,	74	81	92	115	126	134	146	159

the first 10 c.c. of the distillate are shaken with 10 c.c. of standard alcoholic potash, slightly warmed, and allowed to stand for about an hour. Part of the alcoholic solution is then moderately diluted with water, and a solution of lead acetate added. A white precipitate is obtained in the absence of carbon bisulphide, its presence being indicated by the formation of a yellow or yellowish-brown precipitate. This test is, however, not very sensitive. More satisfactory is the sulphocyanide test. It is carried out by treating the first 10 c.c. of the distillate as above mentioned with 10 c.c. of alcoholic ammonia, shaking the mixture, and heating gently. The whole is then evaporated to dryness, the residue taken up with a little water, and with ferric chloride, tested for the presence of sulphocyanides. This test is much more delicate than the first named, but, of course, scarcely suitable for the determination of the quantity of carbon bisulphide present. This is best carried out by means of the hydrazine test, which is also the most satisfactory test for the ready detection of even minute traces of carbon bisulphide.[1] In carrying out this test, a few drops of phenylhydrazine (free base) are added to about 10 c.c. of the solvent, and the mixture is allowed to stand for about two hours. As long as the quantity of carbon bisulphide present is not less than 0·02 per cent., a more or less abundant crystallisation of phenylhydrazine—phenylsulphocarbazinate

$$CS\begin{cases} S.N_2H_2.C_6H_5 \\ N_2H_4.C_6H_5 \end{cases}$$

is obtained. The crystals are filtered off into a weighed Gooch crucible by means of a vacuum pump, 25 c.c. of pure benzol being used for the purpose of washing, and the crucible is then dried for one hour in a vacuum desiccator. The weight of the precipitate may then be ascertained by weighing crucible and contents. By multiplying the quantity of the phenylhydrazine compound thus ascertained by the factor 0·26, the quantity of carbon bisulphide contained in 10 c.c. of the solvent is obtained. This test is much more sensitive than the disagreeable test with triethylphosphine.

The presence of carbon bisulphide in solvent naphtha is objectionable only from the hygienic point of view. As small a quantity as 0·1 per cent. is quite sufficient to make itself noticeable in the atmosphere of even a well-ventilated spreading room, and the baneful effects of carbon bisulphide upon the workers render the absence of this substance in the solvent naphtha absolutely imperative. There is, moreover, no excuse for its presence in solvent naphtha, possessing, as it should do, an initial boiling point considerably above 100° C.

Naphthalene, which was at one time a very frequent impurity in solvent naphtha, now very rarely occurs. Its presence in any appreciable quantity is highly objectionable on account of the very persistent

[1] Liebermann and Seyewetz, *Ber.*, 24, 788.

strong smell it imparts to the manufactured goods. The methods for its detection are obvious.

Pyridine and its higher homologues occur with surprising frequency in solvent naphtha, apparently often escaping the refining process with sulphuric acid. They are objectionable, in the first instance, on account of the extremely acrid and irritating odour they impart to the atmosphere of the spreading rooms, and also on account of their undoubtedly detrimental action upon india rubber. For hygienic and technical reasons it is therefore equally desirable to possess a ready means of detecting their presence in solvent naphtha. This is much more difficult than would at first appear, chiefly owing to the fact that it is practically impossible to completely extract pyridine and its higher homologues from solvent naphtha by means of dilute acids,[1] and the difficulty is further increased by the circumstance that the evaporation of dilute aqueous solutions is impossible without total loss of the pyridine. The following technical test gives, however, entirely satisfactory results, and is of quite sufficient sensitiveness for the purpose.

100 c.c. of the solvent are energetically shaken with 100 c.c. of water in a separating funnel, and the liquids are then allowed to separate. About 15 c.c. of the water are then filtered through a dry filter into a test tube, a few drops of a 10 per cent. solution of cupric sulphate added, and the contents of the test tube heated to boiling point. If the liquid remains perfectly clear, the solvent is either free from pyridine, or its quantity does not reach 1 part in 1500 parts of naphtha (0·06 per cent.). Anything from the faintest to a pronounced bluish-white turbidity, but not leading to an appreciable precipitate of the same colour, after thirty minutes' standing, indicates an amount of pyridine ranging in proportion from 1 : 1500 to 1 : 1000 (0·06 to 0·1 per cent.). If the amount of pyridine present at all exceeds 0·1 per cent., a more or less copious precipitate is obtained. If the amount of pyridine present exceeds 0·3 per cent., turbidity is at once produced in the aqueous extract on adding to it the cupric sulphide. The sensitiveness of this test is exactly coterminous with that of the normal sense of smell for pyridine—*i.e.*, a solvent naphtha, which, according to this test, would be passed as free from pyridine, may, as a matter of fact, contain up to 0·04 or 0·05 per cent. this body; but if so, it cannot be detected either by this test or by the physiological properties of the naphtha as experienced in the manufacturing departments. The presence of so small a quantity as 0·06 per cent. is, however, clearly recognisable by this test, and equally so in the atmosphere of the spreading room.

Adulterations of solvent naphtha by either petroleum spirit or shale spirit are, no doubt, best avoided by purchasing direct from the producers. They betray themselves in most cases already by an impossibly low initial boiling point, and likewise by the lower specific gravity. If a sample of

[1] This, no doubt, finds its explanation in the fact that dilute aqueous solutions of the pyridine salts are almost completely hydrolysed.

solvent naphtha is suspected in this respect, about 50 c.c. of it should be placed in a flask of about 200 c.c. capacity, and connected with a reflux condenser. The flask is well cooled, and a mixture of 50 c.c. of concentrated nitric acid with 50 c.c. of concentrated sulphuric acid slowly added, gently shaking from time to time. As soon as the, at first rather brisk, reaction begins to slacken, water-bath heat is applied for fifteen minutes. The mass is then allowed to cool, carefully diluted with cold water, transferred as completely as possible into a separating funnel, and allowed to settle. The whole of the lower layer is run into a fractionating flask of about 250 c.c. capacity, an excess of aqueous caustic soda is added, and the mass distilled in a current of steam until about one-third of the nitrated bodies have passed over. This operation is repeated with the whole of the distillate for a second time, using a small separating funnel as the receiver, when the unnitrifiable hydrocarbons will be found floating upon the water. The latter is drawn off as completely as possible, and the volume of the unnitrifiable hydrocarbons ascertained by running them into a small graduated cylinder. It must, however, be remembered that even 90's benzol contains invariably from 1 to 2 per cent. of such hydrocarbons, and solvent naphtha from 2 to 6 per cent.

2. **Petroleum Spirit.**—The fractions boiling below 160° C. which are obtained under the name of 'Deodorised Petroleum Spirit' come into the market from the distillation of American crude petroleum. This solvent, in its generally very high state of purity, is used extensively as an india rubber solvent, generally in conjunction with a greater or smaller proportion of coal tar naphtha. Its use without the latter is not satisfactory, as its solvent properties are greatly inferior to that of coal tar naphtha, and also on account of its far greater volatility. Against coal tar naphtha, petroleum spirit has the advantage of being almost odourless, or practically so—a point which, especially in the manufacture of waterproof cloth, is rather important.

Deodorised petroleum spirit consists almost entirely of hydrocarbons of the aliphatic series C_nH_{2n+2}. On submitting it to the boiling point, test figures are obtained, of which samples 9, 10, 11, and 12 in the tables already given are good types. As a matter of fact, however, it will be found that petroleum spirit contains not inconsiderable quantities of much lower boiling hydrocarbons. Indeed, in fractionating large quantities of petroleum spirit (500 gallons at a time), a very large volume of vapours of extremely low boiling point is given off at first, followed by a distillate amounting to about 10 per cent. of the whole, the boiling point of which ranges from about 18° C. to about 40° C., and which, therefore, is evidently a mixture of butane with much pentane.

Of course petroleum spirit of as low a boiling point as the samples above quoted is rather the reverse of advantageous to the manufacturer, and for this reason products like No. 8, and even more so No. 13 and 14, are much preferable.

Besides the boiling point test, petroleum spirit should be tested for the presence of pyridine, and it is also advisable to ascertain whether its purification has been carried far enough. The test for pyridine has already been described above; the purification test is carried out by shaking violently in a test tube 10 c.c. of the spirit with 5 c.c. of sulphuric acid of 1·55 specific gravity. There should be no perceptible amount of discoloration either of the acid or of the hydrocarbon liquid.

There is a general concensus of opinion among india rubber manufacturers that there is greater risk of fire by 'spontaneous ignition' in the use of petroleum spirit, than when coal tar naphtha is employed. This opinion appears to be confirmed by the fire statistics available, which unquestionably show that during the ruling of high coal tar solvent prices, when there is naturally a tendency to use more petroleum spirit in its place, the frequency of fires in rubber factories invariably rises.

3. **Shale Naphtha.**—This is a product produced in large quantities by the Scotch shale distilleries. In its chemical properties this solvent is very similar to petroleum spirit, but while the latter consists practically entirely of hydrocarbons of the aliphatic series, the hydrocarbons of shale naphtha consist almost entirely of olefines. The specific gravity and boiling points of shale naphtha approximate closely to those of coal tar naphtha. Against petroleum spirit it has, however, the disadvantage of a very pronounced and persistent odour. This odour, though highly characteristic, is by no means offensive. Indeed, it is by many considered preferable to the odour of coal tar naphtha, and the preference often expressed for the latter is probably chiefly due to old custom. Wherever the question of odour is of not much account, shale naphtha will be found to be a very effective and cheap solvent for many purposes in connection with the manufacture of india rubber.

4. **Turpentine.**—Turpentine was the first organic solvent which Hancock applied to india rubber in the hope of producing india rubber solutions. In this he failed, ascribing his failure to the impure description of his turpentine. Shortly after his discovery of the effects of mastication upon india rubber, he found that one of the most valuable results of this operation was the readiness with which the rubber so treated dissolved in turpentine—an effect which is, however, just as pronounced with any other solvent. To-day the use of turpentine as a rubber solvent has become almost obsolete save for a few specific purposes. This is, on the one hand, due to its high price (two shillings per gallon); and on the other, to its high boiling point.

It is rather remarkable that all dextro-rotary brands of commercial turpentine are better solvents than the lævo-rotary kinds. For this no doubt very complex phenomenon, no explanation can at present be suggested. Somewhat more intelligible is the fact that the more dipentene a turpentine contains, the better a solvent it is. This in some measure appears to be a contradiction to the first statement, as dipentene is optically

inactive. It is, however, not impossible that the dextro-rotary turpentines contain more dipentene than their optical antagonists. Certain it is that Russian turpentine, the occurrence of dipentene in which is definitely ascertained, and which is also dextro-rotary, surpasses in dissolving power all the other brands of turpentine. The curious old statement that turpentine, after having been distilled over india rubber, acquires thereby much greater dissolving power than before, finds its explanation, perhaps, in the same fact, as it is well known that the distillation of turpentine from retorts heated by direct flame always leads to the formation of more or less dipentene. But in this case the presence of india rubber in the distilling liquid would appear to be quite unnecessary.

5. **Carbon Bisulphide.**—This substance is employed in rubber factories, to a very slight extent only, as a solvent, its volatility, inflammability, and very generally its bad odour being equally objectionable for this purpose. It is, however, employed in enormous quantities as a solvent for chloride of sulphur in the process of cold vulcanisation.

Carbon bisulphide boils at 46° C., and it will generally happen that whatever be the degree of purity of the commercial product, the variations of the boiling point are very insignificant—so much so, that the boiling point in this case practically ceases to be a criterion of the purity of the sample.

The impurities occurring in carbon bisulphide are very little known, especially those that cause the very offensive odour of many of the commercial samples. Free sulphur is almost invariably present, and as long as its amount does not exceed 0·15 grms. in 100 c.c., is quite unobjectionable. For practical purposes the whole of the residue remaining after distillation may be taken to represent sulphur. This, strictly speaking, is not quite correct, and this residual sulphur always contains more or less minute proportions of at least two crystallisable compounds which appear to be to a large extent responsible for the bad odour of the great majority of the commercial products. Besides these, carbon bisulphide often contains sulphuretted hydrogen in solution, and it is scarcely necessary to point out that this occurrence is proof of a very perfunctorily performed purification. Such products are always characterised by a more or less marked yellow colour. The purer a sample of bisulphide of carbon, the more its odour approximates that of chloroform. An acrid or otherwise badly smelling product should unhesitatingly be rejected, as there is no doubt whatever that an article perfectly 'waterwhite' and free from any offensive odour can be and is produced on a commercial scale.

Many attempts have been made to substitute less obnoxious solvents for carbon bisulphide, but although in a few applications pure benzol has proved fairly satisfactory, its general use as the solvent for chloride of sulphur in the cold cure process is barred by the fact that it produces surfaces having a 'starved,' leathery feel, although the vulcanisation, as such, is perfect. This matter has already been discussed (page 80), and it

will suffice here to state that in my own opinion this is due to the fact that the swelling of the rubber is very much less with benzol than with carbon bisulphide. Consequently, in curing a thin rubber film—*e.g.*, waterproof cloth—with benzol as the solvent, only a very slight swelling takes place before the 'setting'—*i.e.*, the pectisation—of the rubber; but under the same conditions, using, however, carbon bisulphide as the solvent, the pectisation of the rubber—in other words, the curing effect—takes place while the film is in a state of considerable distension as regards thickness. I have shown that vulcanisation results in the permanent fixation of the physical condition as to structure of the rubber at the moment at which it occurs, and it is therefore evident that any difference in the physical effect produced by different solvents used in the vulcanisation process must necessarily persist after, and be rendered permanent by, the process of vulcanisation.

This is, in my opinion, the only feasible explanation of the otherwise quite unintelligible fact that, chemically, the process of cold vulcanisation varies considerably in its results according to the nature of the solvent employed. It shows also that the real difficulty of the problem of finding a satisfactory substitute for carbon bisulphide lies not so much, as has been assumed up to the present, in the discovery of some cheap solvent which is fairly volatile and indifferent to india rubber, but rather in finding a solvent, the physical effect of which upon india rubber shall be identical with that of carbon bisulphide.

CHAPTER VII.

COLOURING MATTERS.

Although a great number of india rubber articles are produced having a colour more or less pronounced and differing from that of pure vulcanised india rubber, yet colouring matters do not play a very important part in the manufacture of these goods. The obvious reason is that the uses to which these articles are put are, with very few exceptions only, so highly technical and purely utilitarian as to render their colour a matter of more or less complete indifference. The vast majority of india rubber goods are either grey, black, or red in colour. The grey colour is that of an india rubber article containing no colouring matter of any sort; the black colour is either the colour of desulphurised 'cut sheet' articles, or of goods containing lamp black, pitches, and similar compounds; while the red colour is due to the rubber containing antimony pentasulphide, an excellent sulphur carrier, or it may also be due to the presence in the rubber of nothing more than 'red iron oxide' used for the purpose of imitating the colour of sulphide of antimony, which colour many people still connect with the idea of a very high quality rubber article.

In one branch particularly of the india rubber trade—that of ladies' waterproofs—colours are used extensively for decorative and ornamental purposes, either by producing self-coloured rubber surfaces, or by printing upon variously coloured rubber surfaces textile designs either with ordinary pigment colours, with pigment lakes, or with metallic powders (bronzes).

There is, perhaps, only one other article in which colour is an essential feature. This is in the hard rubber compounds for dental purposes (gums), although obviously in this case the colour serves a utilitarian purpose likewise, being intended to match the colour of the tissues of the mouth. In the production of this 'compound,' Continental and American factories have altogether outstripped their English rivals. The colouring matter employed in this case is invariably either vermilion, the colour of which is attenuated by the admixture of zinc white, or vermilion with a trace of cobalt blue.

In examining any colouring matter intended for use in conjunction with india rubber, the following points call for particular attention:—

1. The colouring matter should contain no substance or compound detrimental to india rubber.

2. The colouring matter should be able to withstand the chemical and physical influences of vulcanisation.

3. The colour in the vulcanised article should be fairly fast to light; it should not bleed on immersion of the article in boiling water rendered faintly alkaline by ammonia, or in water rendered faintly acid by acetic acid.

4. The colour used should not affect the durability of the rubber articles.

White Pigments.

White Lead.—This product is used fairly extensively, owing to its enormous covering power. Its purity may be ascertained by the well-known chemical methods. Seeing, however, that the chief recommendation of white lead lies in its covering power, which is greatly affected by impurities and adulterations, and that even different samples of pure white lead exhibit very considerable variations in this respect, it appears preferable to dispense with the chemical test of this product, and to ascertain its covering power instead, in comparison with some known product of standard excellence. The test is carried out by placing upon a glass plate of convenient size 2 grms. of the standard white lead, and at a distance of from 4 to 6 inches another 2 grms. of the white lead to be examined. To each of these samples 0·2 grm. of lamp black and 20 drops of linseed oil are then added. With a palette knife of suitable size the separate samples are then successively worked by pressing and rubbing, until in each case an absolutely uniformly grey paint is produced, which, by means of the palette knife, is spread in an even coating over the glass. Corresponding to the two samples of white lead so treated, two separate coatings of grey are thus obtained almost side by side, and it is very easy to judge whether they are of identical shade or not. The grey shade produced is, of course, the lighter, the higher the covering power of the white lead. It is now very easy to reduce the darker of the two shades of grey to the shade of the lighter one by gradually working into the darker shade small portions of the same white lead until the two shades are exactly equal. The covering power of the two samples then varies inversely as the quantities of white lead required for the production of identical shades of grey.

White lead is an excellent material for the production of 'cold cured' rubber goods, but it cannot be employed for the manufacture of hot vulcanised articles, the free sulphur at the vulcanising temperature entirely discolouring the white lead. Cold cured goods may also develop this discoloration in a slight degree if the chloride of sulphur employed contains

too much free sulphur, or if the carbon bisulphide used be contaminated with H_2S, or contain too much free sulphur.

Zinc White.—This compound is very extensively employed in the manufacture of white rubber goods. In testing samples it should be remembered that inferior brands often contain sensible quantities of lead or metallic zinc, both of which impurities very detrimentally affect the purity of the colour as it appears after vulcanisation. The covering power of different brands of zinc white is subject to not inconsiderable variations, and should therefore be ascertained by the test above described for the examination of white lead.

Zinc white is equally suitable for the manufacture of cold as of hot cured goods.

The general analysis and valuation of zinc white calls for no special remark, and is carried out by well-known methods. The quantity of metallic zinc or lead contained in it is often so small as to escape detection. It will, however, frequently be found that different brands of zinc white, owing to differences in the quantities of the above named impurities contained therein, exhibit surprising variations in the colour of the rubber goods manufactured by their aid. This is due to the fact that variations in the quantities of these impurities will necessarily also cause variations in the colour of the zinc white as it appears in the india rubber articles after vulcanisation, in which process these impurities are converted into their respective sulphides. The effect of this discoloration can readily be ascertained in any given sample of zinc white by shaking about 2 grms. of it in a test tube with 15 c.c. of water, adding to this suspension one or two drops of ammonium sulphide, and, after two or three minutes' standing, comparing the colour of the zinc white so treated with a suspension of some of the same sample in pure water. Or the zinc white is mixed in a mortar with a small quantity of sulphur, the mixture transferred to a crucible, the sulphur driven off at a gentle heat, and the change of colour noted.

Lithopone.—The theoretical composition of this pigment is expressed by the formula $ZnS, BaSO_4$, and it should therefore contain 29·4 per cent. of zinc sulphide and 70·6 barium sulphate, but most of the commercial products of this description contain much less zinc sulphide. It is a matter of general practical experience that the value of the product as a white pigment rapidly diminishes with the quantity of zinc sulphide present, so that its analysis and valuation resolves itself into the determination of the respective proportions of zinc sulphide and barium sulphate present. This is carried out with sufficient accuracy by dissolving a weighed quantity of the lithopone in dilute hydrochloric acid, adding a moderate quantity of a solution of ammonium chloride, and boiling for from ten to fifteen minutes. The insoluble barium sulphate is filtered off, washed neutral, dried on the filter, the latter subsequently incinerated, and the residue weighed. Deducting the weight thus obtained from the weight of the lithopone used, yields the weight of the zinc sulphide present.

Barium Sulphate.—This is used either in the form of the finely ground mineral 'barytes,' or in the form of artificially precipitated barium sulphate. The latter preparation has a somewhat greater covering power than the natural product, however finely ground. All these, and the following adjuncts, can scarcely be described as white pigments, their whiteness being simply due to the diffused reflexion of extremely fine crystalline, but individually transparent, particles. By embedding these powders in a medium of high refractive index, they become, of course, more or less transparent—*i.e.*, the 'whiteness' disappears. They behave in this manner when incorporated with india rubber, the refractive index of which is comparatively high. They must, therefore, be described as filling agents rather than as white pigments.

Paris White.—This product, also known as whiting, is a more or less impure natural calcium carbonate (chalk). The impurities consist, besides traces of organic matter, of silica (diatoms); in exceptional cases it may contain magnesium carbonate (magnesite), and it invariably contains traces of ferric oxide. It is the most extensively used filling agent; its value as a white pigment is of the slightest.

Red and Brown Pigments.

Golden Sulphide.—This product consists of antimony pentasulphide containing up to 40 per cent. of free sulphur. It is one of the most active 'sulphur carriers' known, but there is little doubt that it was originally employed, and has been extensively used up to the present day, perhaps even more on account of its colour, there being very little choice in red or scarlet pigments suitable for the manufacture of hot cured 'red rubber' goods. The shade of this product varies rather considerably according to the mode of its preparation, and it is very curious to observe that different countries favour different shades, to the practical exclusion of any other. Thus, in France a bright, deep red is preferred, Germany favours a bright orange or tan colour, whilst English manufacturers select a medium shade. For the analysis of this product, *see* page 185.[1]

Vermilion.—This is the most brilliant of all the scarlet pigments available for the purposes of the india rubber manufacturer. It is perhaps the only one which is equally suitable for soft rubber, however cured, as for ebonite. The colour of vermilion varies from a fine but pale bluish-crimson to a full bright scarlet. The shade depends essentially upon the size of the crystals. The smaller these, the paler and bluer the shade; the larger the crystals, the darker and brighter the colour. Adulterations of vermilion are nowadays practically unknown, and it is therefore scarcely ever necessary to proceed to an analysis of it. Under certain circumstances

[1] The frequently made statement that antimony pentasulphide is an excellent vulcanising agent is a pure myth, one of the many to be found in the rubber trade, and as hard to kill as the sea-serpent. The fact of the case is that most of the antimony sulphide in the market contains from 15 to 20 per cent., and more, of free sulphur, to which the supposed vulcanising action of this pigment is to be ascribed.

it may be desirable to ascertain the covering power of a given sample. This is carried out exactly as before described.

Both red antimony sulphide and vermilion proper can be employed for the manufacture of hot or cold vulcanised goods. Their use in the latter case would, however, amount to sheer waste of money, since as good and even much better effects can be obtained with the enormous range of orange, scarlet, and crimson pigment lakes (aniline lakes), which are quite as permanent, and, if competently manufactured for the purpose, perfectly indifferent to india rubber.

Red and Brown Iron Oxides.—These products appear on the market under countless fancy names. Some of the so-called 'Venetian reds' of this class rival in brilliancy and character of shades good qualities of antimony sulphide, but the various products exhibit very great differences in covering power. This is ascertained in the already described manner, and the strongest products should always be given the preference. The reason for this is that ferric oxides, especially the more or less hydrated varieties, are by no means so indifferent to india rubber as is generally supposed. Cold cured india rubber goods containing this article are often found to undergo oxidation rather quickly. This is much less the case in hot cured goods, but there is no doubt that the iron oxide pigments greatly reduce their resiliency.

A complete analysis of these pigments is generally of not much use, as the percentage of iron oxide in them bears only a very remote relation to their intrinsic value. Some of the very brightest 'red oxides' owe, however, the richness of their shade very largely to the presence in them of small quantities of apparently free sulphuric acid. Such products are extremely detrimental to india rubber, and for this reason the neutrality of any given sample should always be ascertained by a special test.

Occasionally brown 'oxides' are offered containing manganese peroxide. The presence of this compound in hot cured goods is highly undesirable and altogether fatal to cold cured goods. This same obnoxious compound is also occasionally encountered in the brown shades bearing the names of umber, sienna, or vegetable brown. Such products call for unhesitating rejection on the part of the rubber chemist.

Red and Brown Lake Pigments.—The very large range of brilliant pigments is almost exclusively prepared from coal tar dyes; a few of them from vegetable dyes. They contain from 5 to 20 per cent. of dye-stuff fixed upon some suitable mineral base. The pigments used for the purposes of the india rubber manufacturer contain these dyes fixed upon either alumina or a mixture of alumina and barium sulphate, or barytes, or white lead, and in some cases even red lead. It is scarcely necessary to remark that pigments containing the latter base should be strictly avoided.

To test for the presence of red lead, the lake is repeatedly boiled with dilute nitric acid, when the appearance of a more or less dark-brown insoluble residue generally sufficiently clearly indicates its occurrence. In

cases of doubt, the residue is boiled with a fresh quantity of nitric acid and a few crystals of oxalic acid or sugar. The ensuing solution is filtered. A white precipitate in the filtrate, on addition of dilute sulphuric acid, indicates the presence of red lead in the pigment.

Aniline Lake Pigments, as these pigments are commonly called, are manufactured from either basic or acid coal tar dyes. Lakes produced from basic dyes are generally brighter and also faster than the lakes obtained from acid dyes, but for scarlet shades the latter yield a far more brilliant series than the former. There is, however, a class of coal tar dyes which may be described as sulphonated basic dyes, and which yield even more brilliant shades than either of the before mentioned classes, although they are perhaps a trifle inferior in fastness to the lakes obtainable from basic dyes. The fastness of all these products both to water and light depends very materially upon the methods by which they have been prepared, but this is scarcely a subject which can be gone into in this place.[1]

Of considerable importance is the question of the action of these lakes upon india rubber. Of course, what action they possess is entirely due to the coal tar dyes contained in them. There is no doubt whatever that some of these have a very distinctly unfavourable action, Bismarck brown having long enjoyed a particularly bad reputation in this respect. This action is certainly greatly reduced in the lake pigments, but it calls, nevertheless, for careful investigation before any particular lake is generally employed in manufacturing—the more so, as it is a practical impossibility to say off-hand what dyes are to be avoided in the form of lake pigments, so much depending upon the manner in which they have been produced. As a general truth, it may, however, be stated that lakes produced from acid dyes are, so far as is known at present, very much safer to use than those manufactured by the use of basic or sulphonated basic dyes. The value of this information is unfortunately largely discounted by the fact that the lakes produced from acid dyes represent only a comparatively limited range of scarlet shades; for all other shades, lakes manufactured from the other classes of dye-stuffs have to be drawn upon. There are, of course, numerous blue, green, and violet acid dyes, but the lakes they form are far too dull for the purpose of the rubber manufacturer.

The valuation of any of these products is best carried out by the covering power test—*i.e.*, by mixing 0·2 grms. of the lake and also of the standard with which it is to be compared with 2 grms. of white lead and 20 drops of linseed oil each upon a glass plate in the manner described for testing the covering power of white lead. This test also gives very trustworthy information respecting the brilliancy of the shade, and renders differences, too slight to be with certainty discernible in the full strength lakes, at once apparent.

[1] Full information on this important subject is to be found in a paper by myself: "Researches on the Formation of Pigment Lakes," *Journ. Soc. Chem. Ind.*, 1891, p. 896; and a further paper under the same title in *Journ. Soc. Chem. Ind.*, 1893, p. 650.

Very frequently dyes soluble in benzene or coal tar naphtha are recommended for the manufacture of coloured india rubber goods. These products, known as aniline resinates, are the resinates of basic dyes precipitated upon a basis of aluminium resinate. They may be used for the manufacture of coloured toy balloons or similar articles, but are useless for general purposes.

All these lake colours can be used for the manufacture of cold cured goods only. In the hot cure process they undergo more or less complete destruction.

Yellow Pigments.

Yellow pigments are only of subordinate importance in the rubber industry. They are occasionally used for toys, and have also been suggested as a means to prevent the 'suncracking' of rubber goods. Their efficiency in this last respect appears, however, doubtful.

Cadmium Yellow is undoubtedly the safest, and also, from the hygienic point of view, the most satisfactory, product to use. It consists of cadmium sulphide, and its shades vary from a deep orange to a rich golden-yellow, according to the conditions under which it was produced. It is undoubtedly the safest yellow pigment to use in connection with india rubber for both cold and hot vulcanising. Whether in the latter process it acts as a sulphur carrier is at least uncertain.

For the valuation of this product it is quite sufficient to ascertain qualitatively its freedom from other metals than cadmium; zinc notably lends itself best to its adulteration. For the rest, the covering power test will give all the necessary information.

Chrome Yellow.—Under this name a wide range of products is known varying in shade from a pale primrose-yellow to a full and almost bright red lead colour. The essential colouring constituent of all these products is lead chromate, and the variations in the shade are due to the presence in them of varying quantities of lead sulphate in the yellower shades, and of lead oxide in the orange and red shades. The presence of lead sulphate is often considered to be an adulteration of the chrome yellow, but if the lead sulphate has been precipitated simultaneously with the chromate, the resulting precipitate has colour qualities which cannot be obtained in any other way. This should be borne in mind when chrome yellows are subjected to analysis. The best test of these, as of all pigments, is to be found, not in their qualitative or quantitative composition, but in their covering power.

Chrome yellows cannot be used for hot cured goods, but behave very well in the cold cure process.

Zinc Yellow, a double salt of zinc chromate and potassium chromate, is distinguished from all chrome yellows by its superior greenish tint, but also by its greatly inferior covering power. It cannot, however, be recommended for use in rubber goods.

Yellow Ochre.—This is a natural product consisting of ferric hydrate deposited upon alumina, silica, or aluminium silicates—generally all three. To the rubber chemist its analysis is without interest, but as some ochres contain the dreaded manganese peroxide, the absence of this compound should be ascertained. In addition to this, an examination of its covering power is all that is required.

All products of this class are equally suitable for hot, as for cold, vulcanised goods.

Yellow Lake Pigments.—There are a number of very brilliant lake pigments derived from coal tar colours, but, like yellow pigments in general, they are little used. The same is the case with the various yellow lakes obtainable from fustic, Persian berries, and other yellow vegetable dyes.

Green Pigments.

Chrome Oxide Green.—This fine green, which should consist of pure chromic oxide, is perhaps the fastest of all mineral pigments. It is not in the least affected in either hot or cold vulcanisation, nor has it the slightest chemical action upon india rubber. Perhaps its only drawback is its comparatively high price. Adulterations of this product are readily detected by ascertaining the percentage of chromic oxide it contains. Its covering power varies according to the care with which it has been prepared.

Brunswick Green (Chrome Green).—The greens which are offered under a variety of other names consist of chrome yellow and Paris blue, and contain generally more or less considerable quantities of mineralic fillings. They are of only limited applicability for india rubber, as they lose considerably in brilliancy in rubber mixings. They stand the cold curing process satisfactorily, but cannot be used for the manufacture of hot cured goods. There is, moreover, a suspicion that they exert some detrimental action upon india rubber. Their analysis is scarcely ever called for, the covering power test readily giving all the required information.

Green Lake Pigments.—A number of very fine green lake pigments are obtainable from the coal tar dyes. The fastness of all of them is very satisfactory, but they can, of course, only be used for the manufacture of cold cured goods.

A large number of green pigment colours exist containing either *copper*, or copper and *arsenic.* It is scarcely necessary to say that all such products are from every point of view highly dangerous. Also the use of the products described as zinc green, mixtures of zinc yellow with Prussian blue, are likely to cause trouble in india rubber.

Blue and Violet Pigments.

Ultramarine.—This blue is on the market in a variety of shades, from ultramarine violet to ultramarine green. It is one of the safest colouring agents to use in india rubber, and will withstand both the hot and the cold

curing process. It is, however, advisable to use only those ultramarine blues which are described as 'alum proof,' otherwise the shade may undergo considerable deterioration, especially in the cold cure process. Its analysis could serve no purpose of the rubber chemist; all the information required concerning any given sample is obtained by ascertaining its covering power, and its behaviour against a 5 per cent. solution of alum. The last named test is carried out by filling two 100 c.c. cylinders with a 5 per cent. alum solution and water respectively, and adding about 2 grms. of the ultramarine to both these liquids. After five hours' standing the cylinders are well shaken and the ultramarine suspensions examined. There should be no change at all observable, or only a very slight one, in the suspension in alum.

Prussian Blue.—This product, which also passes under the name of Chinese blue, is a ferric ferrocyanide, a pigment of a covering power and intensity unsurpassed by any mineral pigment. It has frequently been recommended for the colouring of india rubber goods, but has, so far, not proved of much service in this application. It is produced in a variety of shades ranging from a deep, almost violet blue to a magnificent clear blue of almost the character of an ultramarine (Milori blue). Very little is known as to how these blues behave in the process of vulcanisation, and there has always been some sort of a suspicion that they affect india rubber detrimentally, which would rather suggest that vulcanising agents and conditions are not without effect upon them.

These blues are very commonly adulterated. The quickest way to ascertain their purity, or otherwise, is to digest a sample, which must have been ground into an impalpable powder, for several hours, with a 5 per cent. solution of ammonia until the decomposition is complete. The solution of ferrocyanide is now separated from the insoluble residue by filtration. The filter residue, when washed neutral, should consist of pure ferric hydrate only.

Cobalt Blue (Smalt).—This blue has repeatedly been recommended for colouring india rubber, for which purpose its great indifference to chemical influences would appear to fit it. Its low covering power and very high price have, however, always prevented its general employment.

Blue and Violet Lake Pigments.—There are an abundance of fine blue and violet lakes, which, together with ultramarine, amply and satisfactorily supply all the requirements of the rubber manufacturer in the way of blue pigments. Some care is, nevertheless, required in the choice of the lakes employed, as some of them are rather fugitive, and others have a slight, but none the less distinct, deteriorating effect upon india rubber. It is, however, difficult to single out any particular lakes in this respect, as their behaviour depends very greatly upon the process by which they have been manufactured. It is therefore necessary to conduct a series of experiments with such of these lakes as are selected for use with india rubber.

Black Pigments.

Black pigments are very largely used in the manufacture of rubber goods. The vast majority of these preparations consist of carbon, or contain, at least, carbon as their chief constituent. There are, indeed, some black lake pigments, but these are, however, without any practical importance for the purpose of the rubber manufacturer.

Lamp Black or Vegetable Black.—These products are produced by the imperfect combustion of all kinds of oily materials, and they are always distinguished by their enormous bulkiness, or lightness as it is termed. The fine state of subdivision, which is the chief cause of this property, is, of course, largely responsible for the great covering power of these blacks, but is, however, not an unmixed blessing, as it renders the incorporation of even a moderate proportion of them with india rubber not only a very laborious process, but also one which can only be accomplished by subjecting the india rubber to more or less prolonged mechanical treatment, which is often detrimental to the quality of the articles manufactured from it, and may also cause serious trouble in the process of hot vulcanising such goods. There is further to be considered the fact that each particle of black, as of any other solid substance incorporated with india rubber, carries with it a certain quantity of air into the india rubber, which is only partly eliminated during the mechanical working of the india rubber. Hence it follows that the bulkier the material incorporated, the greater this volume of air, which is distributed throughout the india rubber in bubbles of microscopic minuteness. The porosity thus produced in india rubber articles interferes seriously with the quality of the goods. It is therefore obvious that, as far as pigments are concerned, the denser kinds are much preferable to those possessing great lightness, or bulk. This is especially true of the lamp blacks used in connection with india rubber, and for this reason blacks only should be used, the density of which has been increased by subjecting them, packed into closed crucibles, for several hours to a temperature somewhat above red heat. This treatment has the further advantage of freeing the black from the oily or greasy matters, of which it always contains a more or less considerable proportion. It should also be noted that the colour and depth of shade of the black is vastly improved by this second burning. Altogether, the improvement in every respect produced by this additional process is so great that most of those india rubber works which consume a particularly large quantity of lamp black carry out themselves this second burning or calcining operation.

Bone Black.—This black pigment, which is produced by the charring in closed vessels of bones, is much inferior to the lamp blacks, and its use offers little or no advantage to the rubber manufacturer.

Black pigments should always be analytically controlled in every india rubber works, as the appearance and quality of the goods produced with them depends very much upon their composition and colour qualities. It

has already been stated that lamp black generally contains a certain proportion of oily or greasy matter, not infrequently as much as 12 per cent. and over. This is estimated by extracting a weighed quantity of the black in a Soxhlet extractor. To prevent any of the black passing into the extract, the simplest device is to fill the black in one of the cylindrical filter paper tubes, which can be purchased ready made. Before placing this tube containing the black in the Soxhlet extractor, the open end of the tube is plugged by inserting into it a wad of cotton wool. The extract is collected in a weighed flask. The extraction is effected with either acetone or ether, and after the extraction the solvent is distilled off the flask, the contents of which are then dried in an oven at a temperature not exceeding 80° C., and subsequently weighed.

The only satisfactory way to ascertain the quality of the shade is to observe the shades of grey yielded by the black in admixture with white lead. This test is, of course, included in the ordinary covering power test. The black in this test should produce with the white lead an absolutely neutral grey tint without the least suggestion of a brownish or reddish tint (foxiness). Not infrequently it will be found that a black of an inferior shade has been corrected by adding to it a small quantity of some blue pigment. It is almost invariably Prussian blue which is thus used, and to the experienced eye this sophistication is almost invariably betrayed by the strikingly bluish tint of such blacks, especially after dilution with white lead. Whether such a correction is satisfactory for the more common uses of black pigments we need not discuss here; it is certainly not so to the rubber manufacturer, and blacks of this kind should be rejected. The presence of Prussian blue is readily demonstrated by boiling some of the suspected black with a 10 per cent. solution of sodium dioxalate, when a more or less strongly coloured blue solution is obtained. Should this test fail, the correction may have been effected with either a blue lake pigment, or with ultramarine. The former may be detected by boiling a sample of black with alcohol (85 per cent. strong) acidulated with a few drops of acetic acid, the latter by treating the black with dilute sulphuric acid, when the development of sulphuretted hydrogen can be demonstrated by means of filter paper impregnated with a solution of lead acetate. Should these tests all fail, some of the black embedded in a highly refractive medium, such as Canada balsam or cedar wood oil, is examined under the microscope. Its uniformity, or otherwise, can thus be readily ascertained.

Metallic Lustres (Bronzes).

Impalpable metallic powders, generally misnamed 'bronzes,' have within recent years been extensively employed for the decoration of india rubber goods, more particularly waterproof cloth. They are produced in a very great variety of colours, which are either the colours of the metals or of the alloys of which these powders consist, or which have been obtained by subjecting the finished powders to a dyeing process with aniline colours.

These metallic lustres consist either of copper, tin, or aluminium, or alloys of these with tin, zinc, or occasionally lead; and considering the well-known sensitiveness of india rubber to various metals, a careful selection of the lustre colours to be used in connection with india rubber is of considerable importance. In this respect it is obvious, and, indeed, well recognised, that all those containing copper are strictly to be avoided. There is still some doubt concerning the effects of colours consisting of tin, or of an alloy of this metal, but there is no doubt that under certain conditions even tin may injuriously affect india rubber. On the other hand, it is certain that the metallic powders consisting of pure aluminium are without any action upon india rubber, and this class of lustres, many of them dyed with aniline dyes, are now practically exclusively employed. The avoidance of '*decomposition*' effects ensured by the exclusive use of aluminium was first pointed out in FRANKENBURG'S specification (No. 160, 1896), the date of which, indeed, marks the starting-point of the successful and now very extensively practised application of metallic powders, or lustres, to the ornamentation of india rubber goods.

The question of the nature of the action of the metals upon india rubber will be fully dealt with in a subsequent chapter. Incidentally I may state that the metals, as such, have in no case the slightest action upon india rubber, but a large number of their compounds are more or less injurious.

BURGHARDT[1] was the first to draw attention to the destructive effect of copper upon india rubber. THOMSON[2] arrived at the same conclusion, and made a similar statement with regard to the salts (nitrates) of copper, manganese, and silver; but he found that gold, silver, bismuth, antimony, arsenic, tin, chromium, iron, nickel, cobalt, zinc, and cadmium had no effect, and that lead, aluminium, palladium, and platinum acted only to a very slight degree. This statement of the case is somewhat misleading. The fact of the matter is, that in no case do the metals, *as such*, affect india rubber; but already the sulphides of some of them—notably cupric sulphide, the oxides of gold, silver, tin (stannic), arsenic, nickel, cobalt, manganese, palladium, and platinum—have a more or less marked effect, which is greatly intensified in their salts, particularly such of them as are soluble in water and which act as oxygen carriers. It is, indeed, highly probable that the supposed action of the sulphides, as of some of the oxides, only begins with their transformation into salts under the influence of an impure atmosphere. This, indeed, would account for the fact that copper in waterproof cloth acts far more energetically in cold cured goods than in those cured by the 'dry heat' process. The obvious reason appears to be that the hydrochloric acid vapours, which unavoidably accompany the first named vulcanising process, convert the copper, or rather its oxide, into the chloride, one of the most energetic oxygen carriers. In dry cured goods cupric sulphide would be formed, which would only very slowly undergo oxidation into the much more active sulphate. Accordingly, we

[1] *Journ. Soc. Chem. Ind.* [2] *Proc. Lit. Phil. Soc. of Manchester*, 1890-91.

would have to assume, as a general rule, that metallic contaminations are much more to be guarded against in cold cured than in hot cured goods. This is in perfect agreement with all our practical experience.

It is therefore evident that the employment of even tin or aluminium lustres for the ornamentation of cold cured goods calls for great care in the working if thoroughly satisfactory results are to be ensured. For hot cured goods even these metals cannot be used, as they are considerably tarnished by the sulphur vapours. This is self-evident as regards tin lustres, but might appear unintelligible in the case of aluminium. The explanation is to be found in the fact that commercial aluminium always contains traces of iron, the conversion of which into ferrous sulphide causes the dulleming of the aluminium lustre.

The brilliance of these metallic lustres varies appreciably with the fineness of the metallic flakes, and is the greater, the larger these flakes. It is for this reason necessary to examine these colours microscopically in order to ascertain whether they are of the fineness requisite for the various methods employed for their application to india rubber.

The Dyeing of India Rubber with Soluble Dyes.

It is perhaps scarcely surprising that the very large number of organic natural and artificial dye-stuffs should have stimulated would-be inventors to apply these to india rubber. A great many of the splendid so-called aniline dyes have been tried, their intensity and brilliancy appearing highly suitable for the purpose.

It may at once be stated that the idea of utilising these products for the dyeing of india rubber, as distinguished from staining, suffers from a fundamental misconception, or, rather, complete ignorance, of the nature of the dyeing process—at any rate with the above named dyes.

The dyeing of animal or vegetable fibres with these dye-stuffs is a function of the chemical constitution of both the fibre to be dyed and the dye, and the constitution of either determines the nature of the dyeing process. We find, on the one hand, that any fibre to be capable of being dyed must contain either hydroxyl groups—OH, carboxyl groups—COOH, or amido groups—NH_2, or a combination of all three. On the other hand, we also know that a substance not containing any of these groups cannot be employed as a dye-stuff, although it may possess a strong bright colour.

The case of diazo-benzene $C_6H_5N : NC_6H_5$ is a very familiar illustration of these facts. This body is a fine scarlet colour, but, in spite of this, has no dyeing properties whatever. By introducing into one of two benzene rings either the amido group or the hydroxyl group—$C_6H_5N : NC_6H_4NH_2$, or $C_6H_5N : NC_6H_4OH$—we obtain at once pronounced colouring matters.[1]

[1] A detailed account of the chemical theory of dyeing is to be found in the author's paper—"On Substantive Dyes and Substantive Dyeing: a Contribution to the Theory of Dyeing," *Journ. Soc. Chem. Ind.*, 1894, p. 120.

From these few remarks it follows conclusively that a dyeing of the india rubber—*i.e.*, the formation of a salt-like compound of india rubber and either a dye-acid or a dye-base—is an impossibility, india rubber containing neither hydroxyl, nor carboxyl oxygen, nor amido groups. It might, of course, be objected that this would still leave open the question of the possibility of dyeing india rubber with the mordant dyes—basic dyes on tannin mordant, alizarine on alumina mordant—but the fixing of a mordant upon the textile fibres involves, on the part of the fibre substance, just the same chemical conditions as the fixing of the dyes direct without mordants. The best result which could be obtained on rubber with this class of dyes would be by distributing a suitable mordant uniformly throughout the india rubber, and then dyeing the latter with the corresponding mordant dye. But the result, assuming such a process to be practicable, would be none other than the one far easier and incomparably better attainable—by simply compounding the rubber with a pigment lake consisting of the particular mordant and dye.

Even if we would waive all these weighty chemical objections, there remains the serious difficulty of rendering the india rubber permeable to the dyeing solution, in which water would have to be employed. Dyeing in any other (non-ionisable) solvent is clearly impossible, and not only disadvantageous as MARKFELDT [1] suggests.

There are on the market a considerable number of dye-stuffs which are soluble in turpentine, benzene, and petroleum hydrocarbons. They are offered under a variety of names, and consist either of the stearates of the basic dyes, or of the aluminium resinate lakes of basic or acid dyes. For any process of dyeing, in the legitimate sense of this word, these products are quite unsuitable—indeed, they are no longer dyes, but simply lake pigments soluble in certain organic solvents, and for this reason they do not dye, but only stain. They impart to rubber a characteristic colour only if it is heavily charged with white pigments, or when it is manufactured into extremely thin, and therefore highly transparent, films. Indeed, these products are satisfactory only for the manufacture of stained toy balloons and similar articles.

MARKFELDT actually advocates the use of these products for the colouring of india rubber for waterproofing. The adoption of this suggestion would most certainly prove disastrous to the manufacturer, as all these colours after vulcanisation [2] are more or less liable to 'bleed.' Altogether it may safely be said that the aniline dyes and the above named 'soluble lakes' are useless for dyeing india rubber, and only of very limited use for staining it.

[1] *Gummi Zeitung* [15], 1900, p. 244.
[2] Only the cold cure process could at all be used.

CHAPTER VIII.

CONSTRUCTIVE COMPONENTS OF INDIA RUBBER ARTICLES.

THE applications of india rubber are so extraordinarily numerous and varied that it is scarcely possible to name a single substance used in the arts and industries which, in some form or other, does not find employment as a constructive component of one of the almost innumerable india rubber articles. I do not propose to attempt in this chapter to discuss all the numerous substances which are associated in manufacturing processes with india rubber, but to deal with a few only of these most extensively employed. Undoubtedly the most important of these substances are the textile fabrics which are very generally used either as 'insertions' to give strength to, or limit the distensibility of, sheets, hose, boots and shoes, etc., or simply to produce the various kinds of waterproof goods in which the cloth is the really important part, the india rubber coating being merely an accessory imparting to the cloth the waterproof quality.

The textile fabrics used for constructive purposes proper are fabrics consisting of cotton, jute, or hemp, very rarely wool, and these fabrics are used almost exclusively in the 'grey' state. For waterproofing, cotton, wool, silk, and mixed fabrics are used, which, according to the purpose for which the cloth is intended, are employed in the 'grey' state, but in most cases dyed or printed.

The tests to which these fabrics should be subjected before use vary, therefore, considerably according to the use to which they are to be put. Generally speaking, the textile materials employed for insertions and stiffenings need only be tested for strength before and after exposure to vulcanising temperatures; whereas the fabrics intended for the manufacture of waterproof cloths require also examining for fastness of colour, as well as for the absence of ingredients which are likely to affect the india rubber coating.

Examination of Textile Fabrics.—Insertion cloths are invariably used with a view to strengthen the article to be manufactured, and to reduce its distensibility without destroying its flexibility. The employment of 'insertions' in steam sheeting, pressure, and suction tubing, etc., sufficiently illustrate this. The range of fabrics employed for this purpose varies from very fine 'Cantons' to the coarsest 'ducks,' 'twills,' and 'Hessians.'

The strength of these fabrics is tested by means of a cloth testing machine, of which fig. 18 is an excellent type. It consists of a bed *a*, in which slide the two jaws *b* and *c*. Of these, *b* is connected with the weighting lever *d* and registering dial *e*. Through the lower part of *c* passes the travelling screw *f*, which can be operated by the wheel *g*. The weighting lever is provided with catches *h*, which at any point engage in the notches of the semicircle *i* Any pull on *b* sets the weight, and with it the lever *d*, into motion; but on releasing the pull—*i.e.*, on the material under test breaking—the weight is prevented from falling back by the catches of the lever engaging in the notches of the semicircle, and as the lever actuates

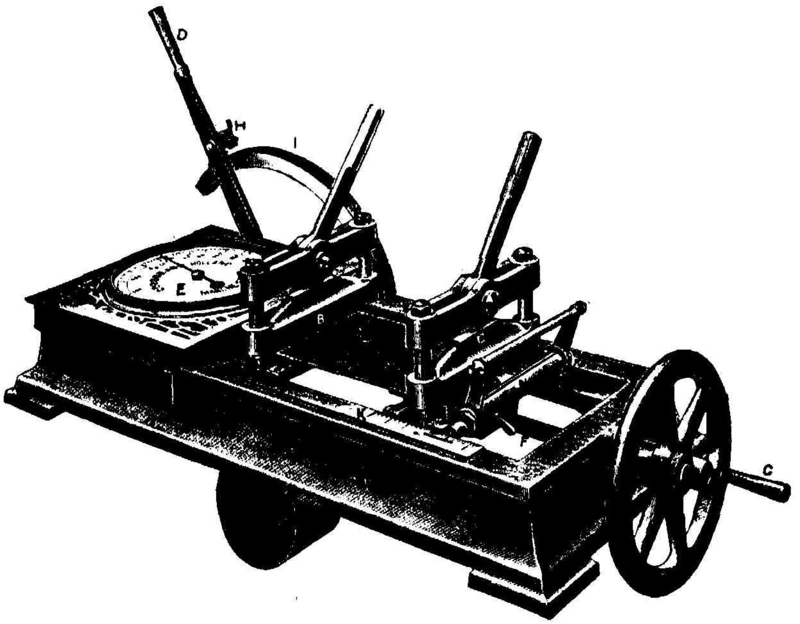

FIG. 18.—Cloth testing machine.

the indicating dial, the index finger of the latter remains stationary at the point where the break occurred.

For the purpose of determining the distension of the material under test at any point, or at its break, the scale *k* is attached to the jaw *b*, which slides upon the bed *a*. Jaw *c* carries a pointer *l*, which determines the exact length of the material under test between the jaws.

It is advisable to carry out all tests with test pieces of the same dimension, so as to obtain all round comparable results. For English practice it will generally be found most satisfactory to adopt the dimensions prescribed in the War Office and Admiralty specifications issued with their forms for tender, viz. :—

The test should always be applied both in the direction of the warp

and in that of the weft of each cloth. It is further very important to repeat this test with two pieces of the same sample which have been exposed to vulcanising conditions, which, as regards temperature and time, are as nearly as possible alike to those subsequently to be observed in the factory. In a very large number of cases a treatment of the samples at 135° C. for two hours will be quite sufficient. The following table gives the results of a few tests obtained with various descriptions of cloths, the tests being tabulated in the manner adopted by the author:—

Description of Cloth.	*Air Dry.*		*After Heating.*		*Tendering.*	
	Warp.	Weft.	Warp.	Weft.	Warp.	Weft.
	lbs.	lbs.	lbs.	lbs.	per cent.	per cent.
Hessian Insertion, . . .	430	397	360	322	16	9
Wigan, ...	280	278	271	272	3	2
Heavy Duck, . . .	320	311	301	303	6	2
Light Cambric, . . .	146	146	132	128	9	12
Cotton Paramatta, . .	94	86	71	62	24	28
Union ,, . .	108	80	97	71	10	9
Wool ,, . .	96	91	90	89	9	2
Gloria Silk, . . .	130	82	111	74	14	9

Determination of Shrinkage.—The determination of the shrinkage of the fabrics used both for insertions and for the manufacture of waterproof tissues will not infrequently be found of value. It is carried out by pouring hot water over a piece of cloth, the length and width of which have been accurately measured, leaving it immersed overnight, and drying it afterwards at a moderate temperature without stretching. The resulting decrease in length and width gives the shrinkage, which is usually expressed in percentages. Shrinkages up to 6 per cent. in either direction are generally found to be unobjectionable. The shrinkage of cotton goods is generally below, that of unions or woollens above, this figure. In very low class woollen fabrics the shrinkage is frequently very considerable.

Determination of the Dressing.—It is quite obvious that the presence of a large amount of dressing or sizing materials in fabrics to be used either as in insertions or for the manufacture of waterproof goods is objectionable, as these materials, without exception, tend to interfere with the adhesion of the india rubber to the fabrics.

In fabrics to be used for insertions, no *dressing*, *sizing*, or *filling* material of any description should be allowed. In the various descriptions of fabrics used for the manufacture of waterproof cloth, the 'finish' of the latter is often a matter of some importance. In many cases it can be obtained only by the aid of foreign materials, and no hard and fast rules can be laid down as to what materials and what quantities should be permitted.

Cotton goods are generally dressed with flour, starch, and similar materials, often with additions of glue, gelatine, tallow, soap, paraffin wax,

zinc chloride, and magnesium chloride. China clay, glycerine, glucose, and Epsom salt are used for weighting.

Woollen goods are dressed with Carraghen moss, gelatine, glue, dextrin, starch, albumen, and sodium silicate.

Silk finishes very commonly contain flea-wort, tragacanth, shellac, and gelatine.

In examining a given fabric for the presence of dressing or filling materials, no detailed analysis is required. For the purpose of the rubber manufacturer it is therefore quite sufficient to first dry a weighed piece of the cloth to be examined in a water oven for a period of at least two hours, and ascertain the loss of moisture by weighing. It is, perhaps, needless to point out that the weighings must be performed in tightly stoppered glass vessels.

The dried fabric is then thoroughly well washed in boiling water, the fingers being used to rub and knead every part of the sample. This washing process is repeated in several changes of hot water. The washed piece is then wrung out and dried in the water oven until the weight ceases to sensibly decrease. The loss in weight is due to the presence of extraneous matter.

There is only one constituent, very commonly occurring in textile fabrics of every description, the amount of which is in every case determined by a special test. This constituent is *tallow*, or *fatty substances* in general, an excessive amount of which is considered to affect the india rubber very injuriously, although, in my own opinion, this danger has been much exaggerated.

The determination of the percentage of fatty matter contained in a given sample of cloth is carried out by first drying it in a water oven for at least two hours. The weight of the dry cloth being ascertained, the latter is transferred to a Soxhlet extractor and extracted with ether or acetone, the extract being collected in a weighed flask. After extraction the solvent is distilled off in a water bath, the flask containing the fatty extract dried for thirty minutes at 90° C., and subsequently weighed.

An amount of 'fatty extract' not exceeding 2 per cent. of the weight of the dried cloth is accepted by the rubber manufacturer as involving no risk to his production. This, however, should not be relied upon too much by the chemist, for while on the one hand, given favourable conditions, this allowance might be, without risk, considerably increased, there is, on the other hand, no doubt that much less than this amount may seriously affect the india rubber, should the cloth at the same time contain slight quantities of copper or manganese. Even certain dyes, notably Bismarck brown, will, in the presence of very small quantities of 'grease,' affect the india rubber very seriously, although in the absence of any fatty matter no perceptible action would have taken place. Nor should the fact be overlooked that different kinds of 'fatty matter' differ very markedly in their action upon india rubber. In this respect it may be stated that

the more pronounced the tendency of a fatty substance towards spontaneous hydrolysis—in other words, to turn rancid—the more energetic is its action upon india rubber.

Examination of the Dyes.—These textile fabrics which are employed in the dyed state, as is the case with the vast majority of the cloths used for the manufacture of waterproof cloth, must always be subjected to an examination respecting the fastness of the colour and of the mordants used in conjunction with the latter.

According to the conditions to which waterproof cloth is subjected in its ultimate use, it is evident that the fastness of the dye to rain, street mud, and dust is essential.

Fastness to Rain.—The obvious test might appear to consist in examining the behaviour of the dye in the course of several hours' immersion in cold distilled water, when the latter should only be very slightly discoloured. No doubt, if all waterproof cloth were worn in the open country only, this test might be considered fairly satisfactory, but the rain falling in large towns differs greatly from distilled water. Amongst the impurities sulphurous acid stands prominent, and although rain water contaminated with this acid does not appear to perceptibly enhance the tendency of dyes to 'bleed,' its effect upon a considerable number of dyes is, nevertheless, very pronounced.

I prefer, therefore, to test the cloth by immersing part of a strip of it in a 0·05 per cent. solution of sulphurous acid in water, wringing out, and drying at a moderate temperature. By comparing the change thereby produced on the immersed part of the strip with the untreated part, much more satisfactory information is gained respecting the behaviour of the cloth in rain than by the distilled water test.

It is impossible to state definitely what degree of discoloration produced in the above test should be obtained to justify the rejection of any given sample for waterproofing purposes. The judgment required for this purpose can only be obtained by practical experience. As a general statement, it may be said that any stain developed in this test becomes the more objectionable, the greater the difference between the shade of the stain and that of the cloth. Reduction of the intensity of the shade, at any rate within certain limits, is therefore much less objectionable than the production of a stain of a different colour.

Resistance to Street Mud and Dust.—The colours of waterproof cloaks are often very badly affected by street mud, more especially that of towns, which, for many reasons, is always distinctly alkaline (ammonia), and invariably contains, besides more or less indifferent mineral detritus, a great deal of organic matter, generally in a decomposed state, and also surprisingly large quantities of iron oxides. The latter are, no doubt, chiefly derived from horse-shoes, human footwear, vehicle tires, and tram rails. It will be readily understood that a complex mixture of this description affects many colours very energetically.

Undoubtedly the most reliable, if not the most elegant, method of testing the fastness of the dye against street mud would be to treat the cloth to be tested with some typical specimen of street mud, allowing it to dry on the cloth, subsequently brushing it off and observing the effect It is preferable, however, to have a test solution which can always be obtained of the same efficiency, and in this respect a 2 per cent. solution of ammonium sulphide answers very satisfactorily. The best way to employ it is to saturate a small part of the cloth with the solution, and to allow it to dry, when its effect can immediately be judged. It must, however, be pointed out that although in a great many cases the effect of this reagent very closely simulates the action of street mud, it does not do this without some notable exceptions. I have particularly observed that with all cloths mordanted or saddened with tannic acid materials, the difference is very considerable, the street mud showing a much greater effect. I believe this to be due to the presence in the latter of iron oxides, or, rather, of soluble salts of iron.

Examination of Mordanting Materials.—Most of the mordanting materials used in the dyeing of textile fabrics are entirely unobjectionable from the point of view of the rubber manufacturer. There are, however, two metals, the presence of which must be carefully guarded against: manganese and copper. Of these two, manganese is now very little used. Its presence is readily detected by boiling a small strip of the suspected cloth with dilute hydrochloric acid, filtering the resulting solution, adding to it excess of ammonium chloride and ammonia, and again filtering. On adding to the filtrate hydrogen peroxide, the presence of manganese is indicated by the immediate formation of hydrated manganic peroxide.

Copper occurs very frequently in dyed fabrics of almost every description, and as extremely small quantities of this metal, or, rather, its oxides and salts, are capable of detrimentally affecting india rubber, the examination of all dyed fabrics for copper is a matter of considerable importance. Enormous losses have frequently been caused by the neglect of this very simple precaution.

With rare exceptions the quantities of copper to be tested for are very small, but although, generally speaking, almost any quantity of copper in cloth intended for proofing is objectionable, it is, nevertheless, desirable to ascertain always the amount present.

This is carried out most expeditiously by means of a colorimetric test, in which the colour of the ammoniacal solution of the copper obtained from a weighed quantity of the cloth is compared with an ammoniacal copper solution of known strength. It is at the outset, therefore, of considerable importance to prepare such an ammoniacal standard solution, the colour of which is certain to keep unaltered for at least twelve months; otherwise, one of the various colorimeters, or LOVIBOND's tintometer, may be employed.

The colour scale is prepared as follows:—About 0·3 grms. of pure

copper foil are dissolved in 5 c.c. of nitric acid (1·4 sp. gr.) and 5 c.c. of concentrated sulphuric acid. This solution is evaporated until the heavy vapours of sulphuric acid begin to appear. The mass is allowed to cool, diluted with 25 c.c. of water and enough ammonia to produce a clear blue solution, which is then further diluted with a mixture of one volume of ammonia with six volumes of water until a solution is obtained containing 0·0005 grms. of copper in 1 c.c.

Next, a set of eight comparison tubes is selected holding 20 c.c. of water without being filled to more than one half, and it is essential that the bores of these tubes should be exactly similar. This is ascertained by placing them in a test tube stand, charging each of them with 20 c.c. of water, and selecting a set of eight of them exhibiting the same height of water column. These tubes are then carefully washed, dried, and charged with 1, 2, 3, 4, 6, 8, 10, 15, and 20 c.c. of the above respectively cupr-ammonium solution, the volumes being made up to 20 c.c. in every case with dilute ammonia (1 : 6), and the tubes finally sealed in the blow-pipe as near the top of the solution as possible. We obtain thus a scale corresponding respectively to 0·005, 0·010, 0·015, 0·020, 0·030, 0·040, 0·050, 0·075, 0·100 per cent. of copper in 10 grms. of substance assayed. These tubes should, of course, be labelled correspondingly.

For the subsequent colour test, 10 grms. of the cloth are ignited in a porcelain basin in a muffle furnace. The basin containing the ash is then allowed to cool, the ash carefully and completely transferred to a small dish, and boiled for a few minutes with a few cubic centimetres of dilute sulphuric acid (5 per cent. H_2SO_4). After addition of an excess of strong ammonia, the liquid is again boiled up and filtered into a test tube of as nearly the same size and calibre as those of the colour scale. The filter residue is washed with dilute ammonia (1 : 6) until the total volume of filtrate, when cold, is exactly 20 c.c. The presence of copper is indicated by a blue coloration, and on comparing its intensity with that of the tubes of the scale, a fair idea of the approximate quantity of copper present is readily obtained. Of course no great accuracy can be claimed for this method, but considering the smallness of the percentages to be tested for, even a considerable percentage error on the result is of little moment.

It is very rare that the percentage of copper exceeds 0·1 per cent., and if it does, it will only be so much more reason for rejecting the particular cloth. Should it be desired, however, to approximately estimate percentages above 0·1 per cent., this can easily be done by taking aliquot parts of the contents of the test tube diluting to 20 c.c. with dilute ammonia, ascertaining the percentage in this diluted solution by means of the colour scale, and multiplying the result by the reciprocal of the aliquot part taken.

The experimental results quoted on page 300 leave no doubt that any cloth containing above 0·005 per cent. of copper should be rejected if the

cloth is to be used for the manufacture of 'cold cured' textures. In cloths used for the manufacture of 'dry heat cured' goods 0·01 per cent. of copper may safely be admitted.

Not infrequently it is stated that fabrics containing chromic oxide Cr_2O_3 are liable to deleteriously affect india rubber. This statement is, however, devoid of any foundation. The oxides, or mordants, capable of destroying india rubber are oxides which, either as such, or particularly in the state of chlorides, act as strong oxidising agents towards unsaturated hydrocarbons, being thereby transformed into subchlorides which are readily reoxidisable by atmospheric oxygen.

Accordingly ferric oxide might be suspected of a similar detrimental action, and, indeed, statements to this effect have sometimes been made, but I have never been able to observe such an influence. Of course it is not at all impossible that under favourable conditions ferric oxide might prove capable of such an action, and the fact of this possibility should certainly be borne in mind. Ferric oxide mixed and vulcanised together with rubber is obviously likely to behave rather differently than when the oxide is only present as a dyeing mordant in the cloth.

Aniline black dyed goods, in the production of which vanadium salts have been used, should be carefully avoided, the merest trace of vanadium being capable of destroying the rubber.

For the detection of vanadium, the cloth is incinerated in the muffle furnace, the ash transferred to a porcelain crucible, covered with a mixture of equal parts of calcined sodium carbonate and sulphur, the crucible covered with a lid and heated until all excess of sulphur has disappeared. The melt is dissolved in a small quantity of water, the solution filtered and decomposed by the addition of a slight excess of hydrochloric acid. A brownish coloration of the ensuing sulphur precipitate indicates the presence of vanadium. The suspended sulphur is precipitated by shaking the liquid with a small quantity of amorphous silica, the precipitate filtered off, dried, burnt off in a porcelain crucible, fused with a few crystals of potassium nitrate, dissolved in water, acidulated with dilute nitric acid, and filtered. If, on addition of a few drops of hydrogen peroxide to the filtrate, a distinct pink coloration appears, the presence of vanadium is proved to a certainty.

Tannic Acid Mordants, which are much employed in dyeing, have no action upon india rubber; but if employed for the production of a range of light fawn or slate shades, they are very apt to cause trouble in another direction. Such cloths, when in wear, often develop numerous spotty or streaky stains of a peculiar dull maroon colour. As spots, they occur particularly at the hem of the garments; as streaks, more particularly on the upper parts. They are caused by almost infinitesimal traces of iron coming in contact with the cloth. The spots round the hem are therefore, no doubt, due to the iron in the street mud; the streaky spots are caused by water, which may be contaminated with iron in a variety of ways.

These stains are extremely unsightly, and once they appear cannot be removed.

The only way to avoid these spots is to reject all fabrics of the above description containing a tannic acid mordant, and since the discoloration is due to the action of iron salts upon the tannic acid mordant, the most satisfactory test is to bring upon the cloth a small drop of a solution of 1 grm. of ferrous sulphate and 1 grm. of ferric chloride in 1000 c.c. of water, and allow it to dry upon a water oven. Any serious discoloration occurring is sufficient justification for the rejection of the cloth.

Amongst the more common defects of india rubber waterproof cloth, the curling of the proofed fabrics is probably the most disagreeable. It is often considered to be due to a shrinkage of the cloth, but this produces the defect known as cockling, also a very unsightly defect. As a matter of fact, the curling defect is always due to either a faulty composition of the rubber mixing employed for the proofing, to a 'curing' fault, or to some omission or commission in the process of proofing (*see* page 303). Quite a number of causes may produce this defect, but the enumeration and discussion of these is a subject for a treatise on the manufacture of india rubber waterproof cloth, which lies outside the scope of the present work.

CHAPTER IX.

ANALYSIS OF INDIA RUBBER ARTICLES.

INDIA RUBBER articles may require investigation for a number of reasons: we may desire simply to ascertain whether successively manufactured batches of goods, of known composition and produced under known conditions, are of uniform quality, or whether they are in accordance with a specified standard; or we may desire to determine the composition of an article in order to reproduce a similar product; or we may desire to ascertain whether an article, the composition of and conditions of manufacture being unknown, fulfils certain specified conditions; or, finally, we may require to ascertain the causes responsible for an article differing from a given standard, or showing a variety of manufacturing defects, or undergoing one or other of the various changes collectively described as 'decomposition.' In all these cases an analysis and general physical examination will be found of the utmost value.

In a number of cases it will be observed that physical tests are the quickest means of gaining the desired information. This applies especially to the control of the production of a factory, or to the comparison of a delivery with a standard sample, and we infer from equal physical constants the chemical equality of the sample tested with the standard. This inference is only admissible with very considerable limitation; as a general statement it is without any truth, and grossly misleading. It is all the more necessary to point this out, as there are still some people who declare the chemical analysis of rubber goods as valueless, and advocate reliance upon the testimony of the physical tests alone. This attitude is due, no doubt, partly to ignorance and inexperience—a still greater part, however, to the fact that an india rubber analysis is at the present moment capable of satisfactory interpretation by those only possessing a long and extensive practical manufacturing experience. The cause of this lies not only in the fact that our chemical knowledge of india rubber is still very imperfect, but also in the circumstance that the physical conditions under which an india rubber article is produced affect its properties quite as much as does its chemical composition. We find, therefore, that although articles produced with the same materials and under identical physical

conditions possess the same physical and chemical constants, it is, as a general principle, equally inadmissible to infer from the identity of the physical tests of different samples their chemical identity, as to pronounce different samples of identical chemical composition to be physically identical.

The course chosen should therefore be adapted to current practice, as, for example, in the iron and steel industry, where the physical tests and the chemical analysis mutually complement each other. This course should recommend itself all the more for general adoption, as it is equally satisfactory in the case of rubber articles chiefly subjected to mechanical wear, as to those subjected to chemical action, or to mechanical and chemical action combined.

Of course the necessity of taking a sample through all the physical tests, and subjecting it at the same time to a full chemical analysis, will hardly ever arise, and it is very easy to decide in the case of any given sample what physical tests to apply, and to what length to carry the chemical analysis. In the vast majority of cases, one or two physical tests, and the determination of two or three of the chemical constituents, are amply sufficient. A full analysis is practically only required when an article has to be produced equal to a sample of unknown composition, or in cases where the causes of the premature break-down or decay of rubber goods have to be investigated. Under such circumstances the complete analysis may become a rather protracted piece of work, but in the former of the above mentioned cases it is a far more rational proceeding to expend a few days of analytical work, instead of taking empirical and random shots in the factory, which are far more expensive and generally much more tedious, and which may or may not be successful. In the investigation of the causes of decay of rubber goods, all physical tests are useless.

(a) Physical Tests for Manufactured India Rubber.

1. **Specific Gravity.**—Time was when the 'specific gravity test' was looked upon as the most reliable guide for judging the quality of a rubber article. The advent of fatty substitutes, the increasing use of resinous and hydrocarbon compounds, of 'ground waste' and reclaimed rubber, has rendered this constant at present almost valueless, and the only inference the low specific gravity of a sample enables us to draw to-day is that it contains little or no mineral matter. Of course this conclusion does not imply that such an article is one of high quality, although there is still a large number of consumers who regard it in this light, and who insist upon having the goods delivered to them of 'floating quality.'

All india rubber articles contain more or less considerable quantities of gases, chiefly nitrogen. It is doubtful whether these gases are dissolved in the india rubber, the probability being that they simply fill the pores, which unavoidably exist in manufactured india rubber, but which are, as a

rule, so minute as to be invisible to the unaided eye. On account of this occlusion of gases, a rubber article possesses a *real* and an *apparent* specific gravity according to the conditions under which this constant is determined. It will further be obvious that the apparent specific gravity is always the lower of the two, and also that all admixtures which tend to increase porosity will increase the difference between the real and the apparent specific gravity. It is therefore very commonly to be observed that a 'floating' rubber article, on careful examination, is found to possess a specific gravity considerably above that of water, so that what keeps it afloat must be evidently the buoyancy due to the presence of occluded gases.

These very simple facts, while showing, on the one hand, the comparative insignificance, or even worthlessness, of the specific gravity test, show us, at the same time, the ratio between the real and the apparent specific gravity to be a very convenient and exact numerical expression of the porosity of a rubber article. This fact has not yet found the practical recognition it deserves, but is thoroughly well worth the careful attention of every rubber worker. The bad behaviour of many india rubber articles in use will be found to be closely connected with their porosity, and I may also state that the addition of small proportions of various (*chiefly organic*) *substances to india rubber mixings—additions* which frequently appear to be utterly worthless factory superstitions—in reality serve the purpose of reducing porosity.

I find it convenient for practical purposes to express this ratio p in the following terms:—

$$p = \left(\frac{\text{real specific gravity}}{\text{apparent specific gravity}} - 1\right) 1000,$$

which, for an absolutely non-porous rubber, would give $p = 0$. The factor 1000 is, of course, introduced simply in order to obtain whole numbers instead of fractions for p.

It will be readily understood that in determining the apparent and the real specific gravity respectively, the samples must be used in such a way, and the tests carried out under such conditions, as to ensure in the former case the retention, and in the latter case the complete expulsion, of all occluded air.

The apparent specific gravity should be determined with pieces of the sample as large as may conveniently be used. These pieces are floated in water in a beaker of suitable dimensions. If the piece floats on the surface, alcohol is gradually added to the water until the test piece remains in suspension at any point in the liquid. The apparent specific gravity of the sample is then identical with the specific gravity of the liquid, which should be ascertained by means of a Mohr's balance. If, on the other hand, the test piece sinks in the water, a concentrated solution of calcium chloride is added until it remains permanently suspended at any part of the liquid mixture. It is scarcely necessary to mention that after every addition of

either alcohol or calcium chloride solution to the water, the mixture should be vigorously stirred.

The real specific gravity should always be determined with the sample in as fine a state of comminution as it is possible to obtain. To attain this, the sample is ground between a pair of steel rollers working at different speeds: a pair of small scale mixing rollers (*see* fig. 22) answer best for the purpose. Where these are not available, working the sample with a very coarse file will often supply suitable material: mere cutting into small strips will not do.

If the sample consists chiefly of rubber with but little foreign admixtures, the sample cannot be 'crumbed' by filing, and even on the above mixing rollers it may occasionally refuse to break up, forming sheets instead. These are, however, always very porous, and if they are only thin enough, cutting them into narrow strips may bring them into a satisfactory condition for testing.

In carrying out the test, an accurately weighed quantity of the sample, prepared as above described, is placed in a pyknometer, the latter filled to about three quarters with distilled water and connected to an air pump. The vacuum treatment is continued until all the air has been expelled. The pyknometer is then completely filled with distilled water previously boiled and brought to standard temperature, and after the insertion of the stopper it is weighed, and the specific gravity of the rubber calculated according to the well-known equation:

$$d = \frac{P}{P_w + P - P_1}$$

P = Weight of the substance (rubber) taken.
P_w = Weight of pyknometer filled with water, at temperature t.
P_1 = Weight of pyknometer filled with water and substance, at temperature t.

It is advisable to use, whenever possible, a quantity of substance amounting to at least one quarter of the weight of the water the pyknometer will hold. Perhaps it is scarcely necessary to mention that in determining the 'porosity' as above described, both the apparent and the real specific gravity must be determined at exactly the same temperature, otherwise serious errors may be committed.

It will be found that the porosity of manufactured india rubber is influenced, not only by the quantity of the admixtures—this is obvious—but very much also by their nature. The effects of the various inorganic filling and colouring materials show very considerable variations, and are in some cases very marked. The highest figures for p are to be found in rubber charged with considerable quantities of rubber substitutes, and recovered rubber.

It must, however, not be assumed that the porosity is a kind of constant of the various admixtures. This is by no means true, as the same mixing proportions give very different 'porosities' with different kinds of india

rubber. The highest figures are always obtained with the 'driest' rubber qualities, the soft varieties giving proportionately lower figures.

The experienced rubber technologist will therefore also readily perceive that the porosity for the same mixing may vary considerably according to the time during which the mixing is worked between the rollers. He will further see that some of the substances frequently used to shorten the time required for mixing by softening the rubber also reduce the porosity of the mixing. Altogether, the determination of p is a test of very wide applicability, and of great utility in the control of operations in the factory.

2. **Mechanical Tests.**—The extremely useful tests known as the 'tensile strength' and the 'elongation' test are carried out on a machine of exactly the same construction as the one shown on page 216. The indicator scale should, however, be so arranged that it stands at zero, when the two jaws are exactly one inch distant from each other, so as to allow sufficient space for the often very considerable elongation of the test pieces.

For the controlling of the production of a rubber factory by means of these tests, it is advisable to use a machine giving readings from four to five pounds up to three or four hundred pounds of tensile strength. On such a machine readings from pound to pound are easily taken, and this is quite accurate enough, providing the test pieces employed are of such dimensions as to give a total minimum reading of not less than a hundred pounds. There is, in the vast majority of cases, scarcely ever any difficulty in fulfilling this condition. This applies likewise to series of test pieces prepared for the study, either of the influence of different vulcanising conditions upon the physical constants of a given mixing, or of the influence of different admixtures under identical vulcanising conditions.

HEINZERLING and PAHL, in their elaborate tables (*see* pages 164–173), express the tensile strength in reference to test pieces of one square millimetre section and hundred millimetres' length. I take it that their data were not obtained from the examination of test pieces of this dimension, but were subsequently arrived at by calculation. This, of course, can be done on the assumption that the tensile strength varies as the sectional area of the test pieces, but that the elongation at break is independent of the dimensions of the test piece, and stands for the same mixing, cured under identical conditions, in a constant ratio to the length actually under test. As a general statement, these assumptions are approximately true, but the approximation in the case of india rubber is none too close. As a matter of fact, according to my own observations, the tensile strength increases in the case of india rubber at a slightly higher rate than the sectional area, and likewise I have found that the elongation or distensibility slightly decreases with an increasing cross section.

Nor is the mere statement of the tensile strength and elongation at break altogether a full statement of the physical behaviour of a test piece under an increasing stress. A far more instructive way of showing the comportment of the test pieces is to measure the stress applied for a number

of successive and increasing elongations, and plot the data thus obtained in the manner shown by the curve tracings in fig. 26. It will be seen at a glance how much more expressive are these curves than merely the two figures above referred to.

3. **Dry and Moist Heat Test.**—These tests are made by exposing the samples for one hour to a 'dry heat' temperature of 270° F., and for three hours to a 'moist heat' temperature of 320° C.[1] The dry heat test is simply carried out in an air bath; for the moist heat test a digester is required, which should be provided with a pressure gauge and thermometer tube (fig. 4).

This test is obviously of some importance in the examination of rubber goods which are to be exposed to heat or high pressure steam, and it is generally supposed to furnish clear indications as to the presence of fatty substitutes in the india rubber. This, within certain limitations, is true of the moist heat test, but a deterioration of a sample in the dry heat test may be due to quite a variety of causes, amongst which the presence of a considerable excess of sulphur should particularly be mentioned.

While it is not to be denied that tests of this description may furnish indications as to the behaviour of an india rubber sample under working conditions, I strongly hold that the indiscriminate application of these tests to all classes of rubber goods is often likely to be mischievous and misleading when, as is often the case, it imposes upon rubber goods test conditions which bear no relation to the conditions under which the goods are used.

4. **Suncracking Test.**—This test does not, strictly speaking, fall under the heading of physical tests, but it finds, nevertheless, a suitable place in this connection.

The liability of india rubber goods of various descriptions, but more particularly tire covers, to develop, often to a very disagreeable degree, the defect known as suncracking, is very generally recognised. It is the result of the oxidation of the india rubber by the atmosphere. The term 'suncracking' might therefore appear to be a misnomer, but, as a matter of fact, it emphasises very expressively the marked hastening of this oxidation under the influence of direct sunlight.

To test the liability of any given sample of india rubber to suncracking, the most satisfactory way would appear to be to expose the sample to the sun's rays for a certain period, perhaps together with some standard sample. This, of course, renders the test dependent upon the weather and season, and at best is a very tedious process, so that it is of some importance to have a more controllable test for this purpose.

Suncracking being, as above stated, due to oxidation, the use of some form of oxygen more active than atmospheric oxygen at once suggests itself. Hence, no doubt, the repeatedly made suggestion to expose the india rubber to the action of ozone. The energetic action of ozone upon

[1] These two tests are collectively known as the 'Admiralty Test.'

india rubber is well known, but it is by no means easy to regularly obtain a gas of the same concentration, and without this the results obtained would be almost worthless.

Of the numerous oxidising agents, nitric acid could not be used, as it not only oxidises india rubber, but also forms nitro and nitroso compounds with it. There is no such objection in the case of chromic acid and the alkaline chromates and permanganates, but the aqueous solutions in which these have to be employed preclude any but the merest surface action. This also applies to aqueous solutions of hydrogen peroxide. It has been stated that an ethereal solution of hydrogen peroxide has a strong action upon india rubber, converting it completely into a resinous mass soluble in alcohol. Unfortunately, however, this statement appears to be devoid of foundation—at least, I have never observed any action whatever of either dilute or concentrated ethereal solutions of hydrogen peroxide upon india rubber.

Some years ago WOLFFENSTEIN[1] described an acetone peroxide $[(CH_3)_2.CO_2]_3$ obtained by the action of hydrogen peroxide upon acetone. This compound dissolved in benzene readily attacks india rubber. In the dry state it is, however, highly explosive, and I prefer, therefore, not to isolate it, but to employ it for the test as follows :—

20 grms. of acetone are mixed with 60 c.c. of 20 per cent. solution of hydrogen peroxide, and the mixture, which will keep unaltered for a long time, is allowed to stand for at least a fortnight before using. The test is then carried out by immersing in this mixture, for a period of at least two days, weighed strips of equal area of both the sample to be tested and the standard with which it is to be compared. After two days' immersion the samples are withdrawn, washed with a little acetone and water, and dried at 100° C. The increase in weight denotes the amount of oxygen absorbed, and is a fairly reliable measure of the relative sun-cracking liability of the sample tested.

I have so far applied this test to the examinations of tire covers only, and the results have proved very trustworthy and in close agreement with the observations on strips exposed to sunlight for prolonged periods.

5. **Electrical Tests.**—The two most important electrical tests in reference to india rubber, and with which every chemist engaged in practical india rubber work ought to be sufficiently familiar to dispense with the assistance of an electrician, are the insulation test and the electrostatic capacity test. These are carried out in the following manner :—

Measurement of Insulation Resistance.

The apparatus required consists of a galvanometer of high sensitiveness. A reflecting galvanometer of the THOMSON type with a resistance of about

[1] *Ber.*, xxviii. p. 2265.

20,000 ohms is preferable, but for many purposes the much less expensive D'ARSONVAL galvanometer will suffice. Either of these galvanometers is worked with any of the well-known forms of transparent scale. In parallel with any of these galvanometers, some convenient shunt is employed, by means of which any desired fraction of the current may be sent through the galvanometer. To determine the constant of the latter, the most convenient arrangement is a megohm resistance. The further appliances required are a battery of at least a hundred cells, a battery key, and a short circuit key, together with two strong, perfectly plane brass plates provided with binding screws.

The first operation is to ascertain the constant of the galvanometer. For this purpose the battery, short circuit key, megohm resistance, and galvanometer are connected in series, the shunt being connected in parallel, with the galvanometer in the manner indicated in the diagram fig. 19.

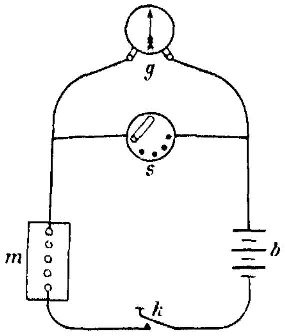

FIG. 19.—Diagram showing disposition of apparatus for taking the galvanometer constant.

In this diagram, *g* represents the reflecting galvanometer, *s* the universal shunt, *b* the battery, *m* the megohm resistance, and *k* the short circuit key. For ordinary practice a reflecting galvanometer of the D'ARSONVAL type possessing a resistance of about 800 ohms is sufficient. The employment of a key in the galvanometer circuit, which is closed only when the short circuit *k* (battery circuit) has been closed, is indispensable.

In taking the constant of the galvanometer, the centre line of the light spot on the screen is brought to zero, the shunt switch turned on the knob marked 1/1000, the battery key closed first, then the galvanometer key. The light spot will move up on the scale, and as soon as it has become stationary, its position is read off. By taking the number of degrees thus read, and multiplying it by 1000 (the dividing value of the shunt), we obtain at once the constant of the galvanometer—*i.e.*, the number of the scale deflection which would have been produced by the battery current acting upon the galvanometer through a resistance of 1 megohm with the shunt at 1, when the whole of the current would pass through the galvanometer.

The constant being ascertained, we can now proceed to measure the insulation resistance of any material. India rubber should be used in the shape of a sheet or film, by substituting it for the megohm resistance in the manner shown in the diagram fig. 20.

In this diagram, *g* again represents the galvanometer, *s* the shunt, *k* the short circuit key, and *b* the battery. The sheet to be tested (*i*) is placed upon the earth plate *e*, which is connected to the wire coming from the short circuit key. Upon the sheet under test is placed the circular brass plate *p*, which is connected to shunt and galvanometer. Surrounding this brass plate is the guard ring *r*, made of brass, which is of larger diameter than the brass plate *p*. This ring is connected to the galvanometer side of the battery through the wire *r'*, and it serves to annul the effect of any surface leakage of current over the surface of the sheet *i*.

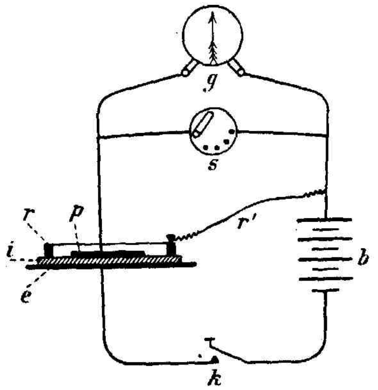

FIG. 20.—Diagram showing disposition of apparatus for determining insulation resistances.

In practice it is also necessary in this case to employ a separate key in the galvanometer circuit. Great care must also be taken to have the shunt switch turned on the 1/1000 knob before closing the battery key, and then to close, in its turn, the galvanometer key.

On depressing the galvanometer key, the light spot on the scale rapidly moves up, and after a few seconds begins to move again slowly backwards. The slower and steadier this backward movement proceeds, the better the insulating material under test, apart from the actual insulation resistance ultimately ascertained. After one minute's electrification, the reading of the position of the spot on the scale is taken.

If the amount of deflection produced is very slight, the shunt switch is shifted to the knobs bearing successively lower dividing values until a distinctly readable deflection is obtained.

The insulation resistance is then calculated in the following manner :— Assuming that in taking our constant we obtain, with the shunt switch at

1/1000, a deflection of 15 degrees on the scale, then the galvanometer constant for a resistance of one megohm is $15 \times 1000 = 15000$. We then remove the megohm resistance, inserting in its place the two brass plates, between which the dielectric material to be tested has been placed. We then put the guard ring *r* in position, concentrically to the round brass plate *p*, and taking care that it is in contact with the dielectric only, and not, at any point, with the lower brass plate. Then we connect the guard ring to the battery arm, as shown in the above illustration.

We place the shunt switch at 1/1000, close the battery key, and subsequently the galvanometer key. If no readable deflection be obtained, the shunt switch is turned on to the next following knob 1/300. Assuming now we obtain a deflection of 9 degrees, the deflection without the shunt would have been $9 \times 300 = 2700$ scale divisions. Now, as the insulation resistance is inversely proportionate to the deflections, the following proportions obtain :—

$$15000 : 2700 :: x : 1,$$

or

$$x = \frac{15000}{2700}$$

$$x = 5{\cdot}5\ \Omega.$$

This figure is, of course, only relative—*i.e.*, it is inversely proportional to the area of the brass plate *p*, but directly proportionate to the thickness of the dielectric. Consequently, in stating the result, the area of that plate and the thickness of the dielectric must be stated at the same time. Thus, if the area of the test plate is 200 sq. cm., the thickness of the sheet 3 mm., the result would be recorded thus :—

Resistance of 'Insulating Compound' per 200 sq. cm. area, 3 mm. thick = $5{\cdot}5\ \Omega$.

Or, if it should be desired to reduce the result to a smaller unit area of the same thickness, this can be done by multiplying the result by the area of the test plate, and dividing the product by the unit area selected.

To ascertain the thickness of such plates or sheets of dielectric materials, the screw micrometer is the most convenient instrument, and is sufficiently accurate. In working with india rubber sheets which have frequently to be tested in the unvulcanised plastic state, the usual form of these instruments with very narrow contact pins is, however, rather unsatisfactory, the readings, owing to the yielding nature of the material to be measured, being liable to be too low. For this reason, that form of micrometer with special broad contact plates, as made for paper makers' use, is much to be preferred. This instrument (*see* fig. 21) should also be provided with a rack work head to prevent the application of undue or variable screw pressure.

The *electromotive force* of the battery to be employed in the above tests depends, of course, materially upon the nature of the dielectric substance to be tested. On the whole, it may be said that the results are the more trustworthy, the higher, within certain limits, the E. M. F. of the testing battery. For tests on india rubber and gutta percha, a battery of from 3 to 400 cells (5 to 600 volts) is generally used ; but in many cases it may

be desirable to employ a lower voltage, and when experimenting with some new material, it is generally advisable to ascertain in a few preliminary tests the most suitable number of cells to employ.

The above described insulation test is, of course, the most important test applied to technical dielectrics, but it is not the only important test. The electrostatic capacity, also the coefficient of self-induction of a dielectric material, are in many cases of almost equal importance, especially in submarine and telephone cables. But as these tests require a very fully equipped electrical laboratory or test room, which is generally under

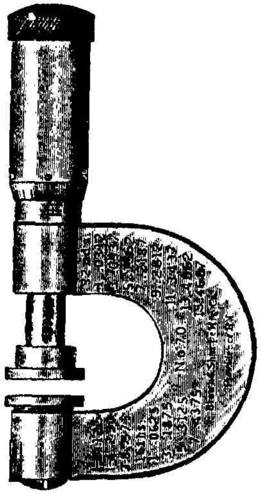

FIG. 21.—Micrometer.

the control of a specialised electrician, their detailed description here would be out of place, and for full information on this subject I refer the student to the larger works on electrical testing.[1] It is certainly indispensable that every chemist interested in the electrical properties of india rubber and its congeners should possess not only a sound theoretical training in electricity, but should also be thoroughly familiar with the practical methods of electrical testing.

(b) CHEMICAL ANALYSIS OF MANUFACTURED INDIA RUBBER.

The great value of the physical tests applied to india rubber articles has long been recognised, but, until comparatively recently, chemical tests were only used in a somewhat random fashion. The analytical investigation of manufactured india rubber, and the analytical control of the works' production, is even at present practised by a few only, and is by some still looked upon merely as a gratuitous attempt on the part of the chemist to supersede the 'practical man,' and to intrude where he is neither competent nor required. This attitude of the 'trade,' unfortunately, does not

[1] KEMPE's *Handbook of Electrical Testing* may be particularly recommended.

even exclude that of a considerable number of the heads of india rubber works. There is no doubt that at the present moment the chemical analysis of india rubber has not yet reached the importance to which it is certain ultimately to attain, but this is largely, if not entirely, due to the fact that our means for the interpretation of the already numerous analytical data which are available are very scanty and inadequate. But this defect is clearly remediable, and its force will become increasingly less as the chemistry of india rubber progresses. Already, at the present moment, chemical analysis is capable of elucidating many of the most difficult and abstruse points with which we are confronted in the manufacture, of often furnishing an explanation of the causes of premature decay in rubber goods, and, in conjunction with the physical tests, of supplying in the fullest manner all the necessary data for the satisfactory control of the production of the factory.

Thus, although at the present moment the advantages of chemical analysis in reference to india rubber are necessarily restricted by our very fragmentary knowledge of india rubber from the purely chemical point of view, this, so far from being an argument for the exclusion of the resources of chemistry from the india rubber industry, should rather act as a stimulant to bring to bear upon the working methods of this great branch of manufacture the possibilities lying in chemical analysis and research, which, in the century just closed, have proved themselves the most powerful agents for quite unexampled developments of old, as for the creation of new, industries.

General Scheme of India Rubber Analysis.

The fundamental difficulty of the analysis of india rubber, as, indeed, of most technical products, lies in the fact that what is required is not an elementary analysis, but a determination of the independent composite substances contained in the manufactured goods. Seeing the almost countless number of substances, both organic and inorganic, which may, with or without some clearly conceived reason, be incorporated in a 'rubber mixing,' it is obvious that in many cases the complete qualitative and quantitative analysis of a rubber article may be a very formidable task, taxing in the highest degree the resources and perseverance of the chemist. Indeed, in many cases the definite qualitative identification, of some of the minor constituents especially, may be quite impossible, and in other cases where we may succeed in identifying a number of these constituents, their quantitative determination may be found impossible. I may, however, at once point out that cases where these difficulties render the analyst's efforts altogether nugatory are of the rarest occurrence. As a matter of fact, the very detection of the presence of such substances which defy exact identification, and consequently also quantitative determination, very frequently gives sufficient indirect information respecting their nature as to lead to their ultimate recognition.

It will be evident that in a very large number of cases there is absolutely no necessity for a full and detailed analysis, and it is frequently quite sufficient to determine the various constituents in groups, or to determine the components of one only of these groups. The objection that india rubber analysis can be accomplished only with an inordinate expenditure of time is therefore quite inadmissible. On the other hand, over and over again it can be observed that weeks of time and considerable *expenditure are wasted in 'practical experiments' in the factory, where an* analysis would have at once solved the whole difficulty.

In its broadest sense the analysis of india rubber consists in the determination of the following five main groups:—

I. India Rubber.
II. Organic Constituents not Rubber.
III. Sulphur.
IV. Chlorine.
V. Inorganic Constituents other than Chlorine and Sulphur.

In actual practice, even in those cases where, for the purpose in view, a division into these broad groups would suffice, the analysis cannot be carried out so as to yield simply the respective proportions in which either of these four groups is present in any given sample. This could only be done in respect of groups III., IV., and V., but the result in respect of the former would be almost worthless unless the absence of sulphuretted substitutes were known with certainty.

The above five groups comprise within them the following subdivisions:—

I. *a.* India Rubber.
b. Recovered India Rubber.
c. Balata.
d. Gutta Percha.

II. *a.* Fatty Substitutes (Sulphides, or Chlorosulphides).
b. Fatty Substitutes (Oxidised or 'Blown' Oils).
c. Free Fatty Oils.
d. Mineral and Resin Oils.
e. Solid Hydrocarbons (Paraffin Wax, Ceresin, Ozokerite).
f. Resins.
g. Pitches (Coal Tar Pitch, Stearine Pitch).
h. Bituminous Bodies (Elastikon, Asphaltum).
i. Carbohydrates (Starch, Cellulose).
k. Organic Bodies not above named.

III. *a.* Sulphur of Vulcanisation.
b. Free Sulphur.
c. Sulphur in Organic Constituents other than Rubber.
d. Sulphur in Inorganic Constituents.

IV. *a.* Chlorine in India Rubber.
b. Chlorine in Fatty Substitutes.

V. *a.* Filling or Weighting Agents.
b. Sulphur Carriers.
c. Colouring Agents (Pigments, Lake Pigments

This list appears formidable, but, as a matter of fact, it is no more so than the list of constituents often ascertained in inorganic analysis. Just as ultimate analysis is simplified through the use of 'group reagents,' so in the same way the constituents of india rubber articles can be separated into groups. We obtain in this manner, in the first instance, a very general view of the composition of the article under analysis, which is then further developed by subdividing these different groups into their several constituents.

The Preparation of the Samples for Analysis.—The procuring of a representative average sample for analysis is one of the most important operations, but certainly also frequently one of the most difficult. The proportion of the various constituents is scarcely ever the same throughout the sample—indeed, it varies often very considerably, alike to the disadvantage of the article as of the analysis. The reason, of course, lies in the difficulty of mixing colloidal masses homogeneously with each other and with the various pulverulent substances employed in rubber compounds.

It is therefore important, in order to obtain a fair average sample, to procure as large a sample of the article to be analysed as possible, and to grind it between a pair of 'mixing rollers.' With rare exceptions all vulcanised rubber goods are thus converted into a mass of fine flakes. This mass, after being well mixed, is again passed through the rollers, an operation which is repeated a number of times, and in this manner a material sufficiently homogeneous for analysis is obtained.

Of course, cutting a strip from end to end from a sample to be analysed, and cutting this into very fine pieces, may serve as an approximation, but it is a very tedious process, and the material is not in such a porous and permeable condition as the above described grinding produces in it. Every laboratory in which much rubber work is done should therefore possess a model mixing roller. This may be worked by hand as long as the width of the rollers does not exceed 6 inches; beyond this, mechanical power is required. Model machines of this kind in various sizes are made by Messrs. J. Robinson, Salford, Manchester, and fig. 22 illustrates a laboratory 'dry-mixer' of their design.

It is scarcely necessary to point out that before passing any rubber articles through this machine, constructive materials, such as cloth insertions, etc., must be carefully removed. This offers little or no difficulty in all those cases where the fabric is completely exposed on one side of the article, as, for instance, in waterproof fabrics or bicycle tire covers. Thoroughly saturating the fabric with benzene is generally quite sufficient to enable its being stripped off the india rubber.

In waterproof cloth it is, in spite of this treatment, often difficult to strip the rubber films, either owing to their extreme thinness, or on account of the films being too weak in consequence of the large amounts of non-rubber constituents they may contain. In this case the simplest

procedure is to saturate the cloth side with benzene, and, as soon as the rubber film begins to shrivel, to place the fabric, rubber face upwards, upon a glass plate, when the 'proofing' can be completely scraped off by means of a good sized palette knife. The rubber obtained from any articles thus treated must, of course, be dried in a water oven before it is further proceeded with.

'Built up' articles—*i.e.*, articles containing rubber mixings of different composition in superposed layers (electric cables, with their 'pure rubber lapping,' 'inner separator,' and 'outer jacket,' are good examples of this class of goods)—should be separated into these respective layers, and each of

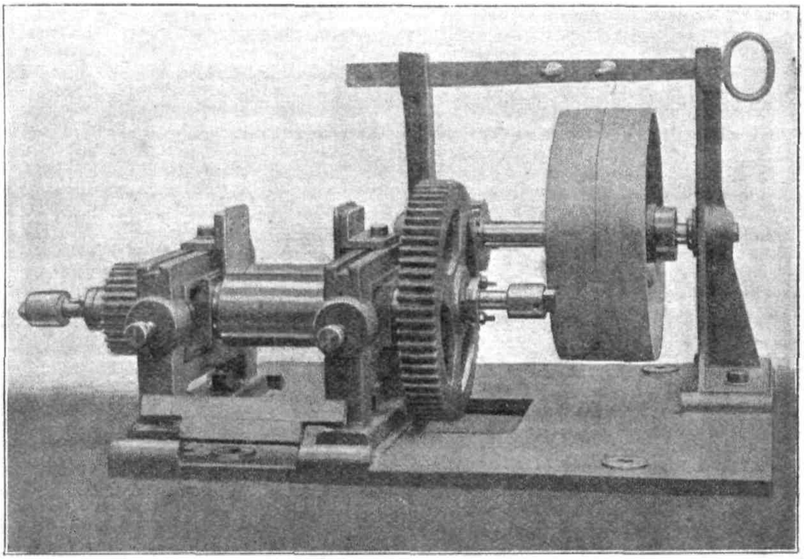

FIG. 22.—Mixing machine (Laboratory scale).

these be analysed separately. In this case it is almost always desirable to determine the ratios of the weights of these different layers to the weight of the whole article. The separation of such layers of different composition may often be accomplished by making a slight starting split with a knife along the plane of union of the two layers, when frequently a practically complete separation may be effected by the exercise of a little patience and some manual dexterity. Occasionally this separation takes place with quite surprising ease, but quite as often it may be found utterly impracticable, and in this case a tedious dissection by means of a sharp knife is the only means available. This, of course, renders a determination of the weight ratios of the different layers by the above suggested process practically impossible, but a very satisfactory and accurate way of obtaining these data consists in the preparation of a

cross section of the sample, measuring the exact thickness of each layer (either macroscopically or microscopically, according to the thickness of the object), and multiplying the thicknesses measured by the specific gravities of the respective layers. The figures thus obtained are exactly the desired ratios.

The samples prepared for analysis should be kept in air-tight bottles, which should not be exposed unnecessarily to daylight, and never to direct sunlight. Samples which are to be preserved for future reference, particularly those which are or may become objects of legal proceedings, must be preserved in sealed glass tubes.

Analytical Methods.—A brief glance at the list of the chief constituents to be met with in manufactured india rubber shows that they may contain quite a number of substances soluble in neutral organic solvents of low boiling points. Some, indeed, contain substances (inorganic salts,[1] dextrine) soluble in water, but these cases are rare. It may therefore occasionally be of importance to boil a small quantity of the sample with water, determine the reaction of the solution, and ascertain whether, after having been filtered, it leaves a residue which can be further examined. If the water shows an acid reaction, this is generally due to the sample having been vulcanised with sulphur monochloride. Very frequent also is the presence of sodium chloride in the aqueous extract, as this is a very frequent constituent of 'white substitute,' in the manufacture of which sodium bicarbonate has been employed.

The treatment of india rubber with organic solvent requires some consideration. Carbon bisulphide and benzene are excellent solvents for free fatty and mineral oils, solid hydrocarbons, and similar substances. At the same time, they are, however, also solvents for india rubber and its congeners, and although vulcanised india rubber is practically insoluble in all solvents, this is, strictly speaking, only true in those cases where the india rubber is fully vulcanised. Even more serious is the fact that many of the 'brown substitutes' yield to these solvents considerably more than the free fatty oils they contain. This is, of course, a serious objection, as their employment would result in the appearance of these bodies in two different analytical groups.

The alcoholic solvents are free from these objections, but they are very bad solvents for the hydrocarbon oils, although, on the other hand, they are on the whole good solvents for the resins, or, at least, of those which are used in the manufacture of india rubber goods.

Acetone is, however, the solvent which is free from any of the objections applying to the above named solvents. It will, particularly at higher temperatures, easily dissolve all the oily and resinous constituents of india rubber, gutta percha, and Balata without dissolving a trace of any of these last named bodies themselves. It also readily dissolves free fatty oils,

[1] I have found goods containing as much as 6 per cent. sodium carbonate, though what the merit of this addition is supposed to be I have never been able to ascertain.

mineral oils, solid hydrocarbons, resins, and the free sulphur. For this reason I have made use of this solvent for years, and always found it to answer most satisfactorily.

In carrying out the extraction of an india rubber sample with acetone, from 1·5 to 2 grms. of the sample are placed in one of Schleicher and Schüll's extraction thimbles, which is inserted in the extractor. The type of extractor to be used is a matter of some importance, as upon this depends to a considerable degree the rapidity with which the extraction may be completed. The most generally used form of extraction apparatus is the one devised by Soxhlet, and as long as its capacity does not exceed from

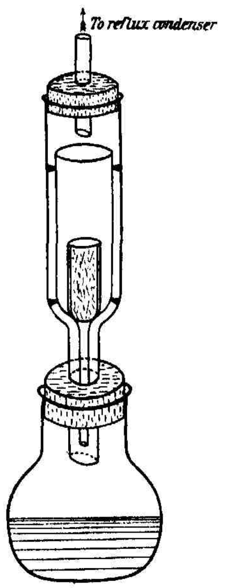

FIG. 23.—Apparatus for the extraction of india rubber samples.

50 to 60 c.c., it answers fairly well, but for our purpose I very much prefer a form of extractor in which an inner tube, which receives the thimble, fits into an outer jacket, so that there remains a free annular space between them through which the vapour of the extracting liquid may pass up into the reflux condenser, thus keeping the material to be extracted always at the temperature of the boiling liquid. Care need only be taken to arrange the tube leading from the reflux condenser to the inner extractor tube in such a way that the condensed solvent falls straight into the thimble containing the material to be extracted. In this apparatus even the most refractory sample can be extracted in less than five hours, whereas about double that time is required if a Soxhlet apparatus be used.

The whole of the apparatus is shown in working order at fig. 23.

The separation effected by this extraction in reference to our list of constituents on page 236 is as follows:—

A.—Extract.	B.—Residue.
I. Oily and Resinous Constituents of India Rubber.	I. India Rubber, Gutta Percha, Balata.
II. Free Oils from Substitutes. Free Fatty Oils. Mineral and Resin Oils. Solid Hydrocarbons. Resins. Organic Bodies not named above (?).	II. Chlorosulphide Substitutes. Sulphide Substitutes. Oxidised or 'Blown' Oils. Pitches, Tar. Bituminous Bodies. Carbohydrates. Organic Bodies not named above (?).
III. Free Sulphur.	III. Sulphur of Vulcanisation. Sulphur in Organic Constituents other than Rubber. Sulphur in Inorganic Constituents.
	IV. Chlorine in India Rubber. Chlorine in Fatty Substitutes.
	V. All Inorganic Constituents.

It will at once be seen that the complete analysis of this extract may be a very difficult matter—indeed, it may safely be said that our present day methods would be utterly inadequate for the analytical disentangling of such a mixture, this being particularly so in view of the fact that the quantities of substance on which this would have to be done rarely exceed 10 per cent. of the rubber sample.

There is, however, scarcely ever any need for a complete analysis of this extract, an investigation of its general characteristics yielding sufficient indication respecting its nature.

If the extract forms a more or less viscous liquid, it may be taken for certain that it does not contain any solid hydrocarbons or resins, both of which, even in small quantities, deprive fatty and mineral oils of their fluidity.

If, on warming the extract with about 5 c.c. of absolute alcohol, there remains a liquid residue, this consists of mineral oils. If the warm alcohol on cooling deposits voluminous flakes, the presence of solid hydrocarbons (paraffin wax, ceresin, ozokerite) is a practical certainty.

A rough estimation of the fatty oils present may be effected by extracting at least 10 grms. of the sample, saponifying the extract with 25 c.c. of standard alcoholic caustic potash, and titrating back with standard hydrochloric acid.[1] As the fatty oils present, in nine out of ten cases, consist of colza oil, we may assume that every 172 mgrms. of caustic potash which has disappeared in the saponification represents 1 grm. of the fatty oil present.

In the presence of a composite extract, the determination of the amount of extract derived from the india rubber is an absolute impossibility, largely owing to the very indifferent character of the soluble matter contained in india

[1] This is practically the KOETTSTORFER test.

rubber. A very little experience will suffice to enable the worker to judge from the appearance of an extract as to whether it is derived from india rubber solely, or whether it is contaminated with one of the other substances named in schedule A.

Of course the acetone extract also contains the whole of the free sulphur present, the amount of which in the various india rubber articles may vary from nothing to 20 per cent. and more. In rubber analyses pretending to the highest attainable degree of accuracy, the weight of the free sulphur must, of course, be deducted from the weight of the total acetone extract. If the free sulphur separates out in the extract in the form of well-shaped crystals, this is an unmistakable sign of the absence of oily or resinous ingredients other than those derived from india rubber, or of solid hydrocarbons, in the extract. In this case the acetone is distilled off, the flask dried in a water oven, and the weight of the total dry extract ascertained. The dry extract is then treated five times in succession with increments of 2 c.c. of acetone, and these washings are filtered through a small filter into a weighed flask. As this filter may contain a few crystals of sulphur, it is placed in the original flask and washed with 5 c.c. of carbon bisulphide. After the solvents have been driven off on the water bath, the two flasks are dried, and their contents of organic extract and sulphur ascertained respectively by weighing.

This method involves an error due to the solubility of sulphur in acetone. This error is represented by from 5 to 6 mgrms. of sulphur dissolving in the 10 c.c. of acetone used for the above separation, and it is therefore necessary to increase the amount of sulphur, and to reduce the organic extract by this amount in the subsequent calculations.

If the extract is of a highly composite nature, and especially if solid hydrocarbons are present, the above method for the estimation of the free sulphur cannot be employed. If, nevertheless, its direct estimation be deemed important, it may be effected by oxidising the whole of the acetone extract with fuming nitric acid on the water bath, diluting with water, filtering and washing, and finally precipitating the sulphuric acid formed as barium sulphate.

For the detection and determination of tar, pitches, and bituminous bodies (asphaltum) in india rubber, Henriques proposed to treat the sample in the cold on a filter with nitrobenzene. If freshly distilled, and therefore very pale-coloured, nitrobenzene is used, this method allows us to detect the presence of the above bodies by the dark colour of the nitrobenzene passing through the filter. In the presence of tar or pitches the colour of the filtrate is a brownish-black; asphaltum dissolves with a characteristic rich mahogany colour. The direct gravimetric estimation of the substances present in the extract is, however, impossible owing to the very high boiling point of nitrobenzene.

Henriques' process consists in treating 1 grm. of the sample with 30 c.c. of nitrobenzene at the ordinary temperature in a small beaker for about

one hour. The mass is then transferred to a filter, and the solvent squeezed out as much as possible by pressing it with a small pestle. It is then washed with another 30 c.c. of nitrobenzene. The residue is then washed with water into a porcelain basin and boiled with water until all the nitrobenzene has disappeared. The washed mass is then dried and weighed, the loss consisting of the above named bodies.

According to Henriques, tar, pitch, and asphaltum are completely soluble in nitrobenzene. As a general statement, this is certainly not correct. Very frequently these bodies contain a not inconsiderable amount of insoluble matter which is not extracted in the above treatment. This is not of much account, as the amount of these substances used in rubber mixings is, as far as my experience goes, always very small, scarcely ever exceeding 2 per cent. Samples like those quoted by Henriques, containing respectively 8, 21, and 14 per cent. of asphaltum, I have never met with, and I doubt very much whether they represent *bonâ fide* manufactures.

I look, nevertheless, upon the direct estimation of these bodies as a matter of some importance, as, in the first instance, their employment in a 'mixing' must always be regarded as a matter of not inconsiderable technical significance. Moreover, as all asphaltum contains from 3 to 10 per cent. of combined sulphur, the estimation of the latter can rarely be neglected, and this estimation is only possible if we get the actual extract, free from its solvent, to deal with.

This I carry out by following up the extraction with acetone by an extraction with pyridine without any intervening drying of the paper cone and its contents. After removing from the extractor the flask containing the acetone extract, I therefore at once connect the extractor with a weighed flask containing about 60 c.c. of pyridine (B.P. 109 to 111° C.).[1] This flask I heat in an oil bath, the temperature of which is kept between 116 and 120° C. In the presence of tar, pitch, or asphaltum, the paper at once assumes a more or less pronounced brown colour, and I continue extraction until it has assumed its normal tint. I then distil the pyridine off on an oil bath, the temperature of which is again kept at from 116 to 120° C. The employment of a sand bath is inadvisable on account of the risk of overheating towards the end of the distillation.

On removing the flask from the oil bath, it is carefully cleaned with filter paper, and finally with filter paper moistened with benzene. The flask is then heated in a water oven until the smell of pyridine has disappeared. Subsequently the weight of the extract is ascertained.

Whether the extract consists of tar, pitch, or asphaltum may generally be decided by an examination of the consistency and colour of the extract, tar being a black viscid liquid, pitch a ductile black mass, and asphaltum a brittle, very dark brownish-maroon substance. A mixture of any two of these substances would be extremely difficult to detect. But this is scarcely of any account, as the employment of such a mixture would be

[1] Pure pyridine boils at 116° C.

due to the individual fancy of the manufacturer rather than to any particular virtue of the blend.

The addition of all these substances to rubber mixings only serves the purpose of softening the india rubber without subjecting it to an undue and detrimental amount of mechanical working. This softening may be desirable, either for the purpose of enabling the rubber to take up readily large quantities of mineral matter, or to assist in any subsequent calendering of the rubber mixing.

The separation we have effected by this pyridine extraction is shown in the following schedules :—

C.—Extract.	D.—Residue.
	I. India Rubber, Gutta Percha, Balata.
II. Tar. Pitch. Bituminous Bodies.	II. Chlorosulphide Substitutes. Sulphide Substitutes. Oxidised or 'Blown' Oils. Carbohydrates.
III. Sulphur in Extract.	III. Sulphur of Vulcanisation. Sulphur in Organic Constituents other than Rubber. Sulphur in Inorganic Constituents.
	IV. Chlorine in India Rubber. Chlorine in Fatty Substitutes.
	V. Inorganic Constituents.

The estimation of the sulphur in all the various forms in which it may appear in manufactured india rubber is one of the most important points in the complete analysis of a rubber article. We must, therefore, also test for sulphur in the pyridine extract (C), and if any be present, determine its amount quantitatively. The sulphur in this case cannot be present in the free state, but only in organic combination, for it cannot be estimated by the method adopted for its determination in the acetone extract, owing to the frequent conversion of these organic sulphides, partially at least, into sulpho-acids, the barium salts of which are soluble in dilute hydrochloric acid. The following procedure is therefore adopted :—

The pyridine extract is oxidised on the water bath with fuming nitric acid in the flask in which it was weighed. As soon as complete solution is obtained, it is transferred to a porcelain incinerating dish of about 6 cm. diameter. The flask is then washed with hot fuming nitric acid, the washings being added to the contents of the dish. The whole is now concentrated to a syrupy consistency, about half a grm. of pure sodium acetate is added, and evaporation continued to dryness. The dry residue is ignited over a Bunsen burner, the carbonaceous mass completely oxidised by slowly adding the requisite quantity of sodium nitrate, and the mass allowed to cool. It is then dissolved in hot water, the solution filtered,

and the filter washed neutral with water. After acidulating the filtrate with hydrochloric acid, the sulphuric acid is precipitated, and its amount ascertained in the usual manner.

We proceed now to determine in the residue from the pyridine extraction (D) the amount of fatty substitutes present. This is carried out by the very simple and satisfactory method due to HENRIQUES, and which is based upon the fact that all these substitutes are still essentially triglycerides, and, as such, saponifiable with caustic soda or potash.

Before applying this saponification test, the residue D is freed from all adhering pyridine by washing it in the extraction thimble with acetone. It is then dried, weighed, completely transferred to a wide-necked flask, and after addition of 25 c.c. of alcoholic caustic potash or soda, heated upon the water bath on a reflux condenser for from three to four hours. In important cases it is advisable to repeat this treatment with a fresh lot of caustic potash. All the alcoholic liquors are carefully collected, the insoluble residue washed upon a filter with boiling water, and completely freed from alkali by washing with water. All these washings are united with the alcoholic saponification liquors.

The filter residue is dried in a water oven in a current of coal gas. This is best carried out by placing the residue in a weighed wide-necked flask provided with a doubly perforated cork stopper. Through these perforations pass two short pieces of glass tubing. The one of these is connected to the gas supply, the other to the Bunsen burner, heating the bath by means of india rubber tubing which is passed into the oven through its aperture at the top. The residue is thus dried in a current of coal gas to avoid oxidation, which, without this precaution, might affect the final result to a very considerable extent. The dry residue is finally weighed in the flask, and the loss of weight very accurately represents the weight of the fatty substitutes removed by saponification. The percentage represented by this amount must, of course, just as all the previously ascertained data, be calculated upon the original weight of the sample taken, and not upon the weight of the residue from the pyridine extraction.

According to HENRIQUES, the above described method for the determination of the fatty substitutes is liable to be vitiated by the fact that the india rubber retains as much as 6 per cent. of its weight of caustic potash in an insoluble condition, and he states that this alkali can only be removed by boiling the india rubber with dilute hydrochloric acid. Of course there is no objection to this treatment in the case of india rubber free from mineral matter, or of india rubber free from mineral matter soluble in hydrochloric acid. But, as a rule, the greater part of the mineral matter used in rubber mixings is soluble in hydrochloric acid; others are partially soluble, undergoing decomposition under the influence of the acid. It will readily be perceived that in such cases this treatment would very considerably complicate the determination of the mineral

constituents of the rubber articles, all the more so as the complete removal from india rubber even of those inorganic bodies which are easily soluble in hydrochloric acid is an extremely tedious operation. I have found, however, that the absorption of alkali by the india rubber is not what would appear to be a somewhat obscure function of the india rubber itself, but is entirely due to the presence of resinous bodies in the latter. If these are removed before the application of the above described saponification process, the absorption of alkali by the india rubber is too insignificant as to call either for HENRIQUES' hydrochloric acid treatment, or for any other correction. But this is exactly what our first operation, the extraction with acetone, accomplishes.

The fatty substitutes extracted are either chlorosulphides, sulphides, or oxides of triglycerides, and it is generally of importance to ascertain which of these is present. Not infrequently two of these substitutes are used in rubber mixings, but which of them can be discovered fairly approximately only by a quantitative estimation of the amount of chlorine and sulphur present in the saponification liquors; and as these figures are also of importance in respect to the question of the vulcanisation of the rubber sample under examination, their determination becomes almost invariably necessary.

This I carry out by evaporating the whole of the washings which have been collected from the saponification process, in a porcelain basin, to a volume of about 50 c.c. This is then made up to 100 c.c. with water in a graduated cylinder, the water which has to be added being used to wash the basin. I then take 50 c.c. of this solution, evaporate it to dryness in an incinerating dish, ignite over a Bunsen burner, oxidise the carbonaceous matter by the careful addition of sodium nitrate, dissolve the subsequently resulting mass in water, acidulate with nitric acid, and add silver nitrate. Any precipitate of silver chloride thus obtained is filtered off, treated in the usual manner, and weighed. The amount of chlorine thus found must, of course, be doubled.

The other 50 c.c. of the above solution are first oxidised on the water bath with bromine, or bromine water, in order to oxidise the alkaline sulphides present, and are then concentrated by evaporation to the state of a syrupy liquid, which is oxidised with fuming nitric acid, evaporated to dryness and ignited, finally also being fused with sodium nitrate. The resulting mass is dissolved in water, and the sulphuric acid present determined in the usual manner. It is obvious that the amount of sulphur thus ascertained must also be doubled.

If there are chlorine and sulphur present, it will generally be found that their respective amounts appear approximately in the ratio of their molecular weights. In this case the fatty substitute present is either the chlorosulphide of one of the unsaturated fatty oils (colza oil)—*i.e.*, 'white substitute'—or a mixture of the latter with one of the 'blown' oil substitutes.

If there are both chlorine and sulphur present, but the latter considerably in excess of the above stated ratio, this is evidence that the fatty substitutes employed are a mixture of 'white' and 'brown' substitute, or perhaps even of these two with a 'blown' oil substitute.

The presence of sulphur only indicates the presence of either 'brown' substitute alone, or a mixture of it with 'blown' oil substitute.

The absence of both chlorine and sulphur proves the substitute present to consist entirely of 'blown' oil substitute.

Further information on this point will be found in the next chapter, but attention may already here be drawn to the fact that if 'white' substitute, as is frequently the case, is employed in the manufacture of hot vulcanised goods, it loses a more or less considerable proportion of its chlorine in the form of hydrochloric acid. HENRIQUES assumed that in this case the hydrochloric acid escapes altogether during the process of vulcanising. This assumption is, however, entirely erroneous. The hydrochloric acid eliminated from the substitute is retained entirely by the india rubber, with which it combines to form polyprene hydrochloride, and it is also probable that some part of it, in the presence notably of litharge or calcium carbonate, combines with these. But as the de-chlorination of the 'white' substitute under the conditions mentioned is far from complete, the presence of chlorine in the substitute cannot escape detection.

The saponification of the residue D with caustic alcoholic potash has therefore resulted in the following further separation :—

E.—Extract.	F.—Residue.
	I. India Rubber, Gutta Percha, Balata.
II. Chlorosulphide Substitutes. Sulphide Substitutes. Oxidised or 'Blown' Oils.	II. Carbohydrates.
III. Sulphur in Fatty Substitutes. Chlorine in Fatty Substitutes.	III. Sulphur of Vulcanisation. Sulphur in Inorganic Constituents.
	IV. Chlorine in India Rubber.
	V. Inorganic Constituents.

For the separation of the india rubber from the mineral matter, HENRIQUES proposed to employ the solvent action of boiling petroleum, or, rather, of those fractions of petroleum spirit boiling above 150° C. This is, however, an extremely unsatisfactory process, as the solvent named will attack very lightly vulcanised india rubber only. I subsequently suggested, and until quite recently practised, the use of boiling nitrobenzene, which is a far more powerful solvent, and yields solutions which are rather easier to deal with than those obtained by the aid of petroleum. But even this solvent is not capable of resolving satisfactorily samples possessing a vulcanisation coefficient exceeding 4 per cent. of sulphur, and the number of

such being rather large, the limitations of this process were often very restrictive.

There remained, then, only the determination of the mineral matter by the most obvious process—namely, incineration. But to this process attaches the very serious objection that it interferes with the composition of the inorganic substances present in such a manner as to render altogether impossible the determination of the exact nature of the mineral substances added to the rubber mixing. Any mercury compounds volatilise altogether; sulphides are converted into oxides or sulphates; carbonates lose their carbonic acid; oxides are converted into sulphides, which may then undergo further oxidation; carbon pigments, carbohydrates, animal and vegetable fibres are burnt off, and thus often unavoidably accounted for as 'india rubber.' As a rapid control for works' purposes, the incineration test answers in the majority of cases well enough, but in the analysis of samples of unknown composition it is entirely unsatisfactory.

Quite recently I have succeeded in finding a far more effective resolvent for even highly vulcanised india rubber than nitrobenzene. This substance is α-nitro-naphthalene. The readiness with which this body resolves india rubber possessing a vulcanisation coefficient of from 2 to 8 per cent. is perfectly surprising; even samples showing vulcanisation coefficients up to 15 per cent. are quickly and completely decomposed at a temperature of from 170 to 180° C. The solutions obtained in the nitrobenzene treatment are often extremely difficult to deal with, the mineral matter absolutely refusing to settle out,[1] and forming often practically unfilterable solutions. On the other hand, the solutions obtained in the nitro-naphthalene treatment, after dilution with benzene, and after a few hours' standing, filter very readily, and yield clear filtrates.

The only peculiarity the nitro-naphthalene treatment presents is one it shares with the nitrobenzene treatment—*viz.*, that if it is applied to substances containing either red lead or ferric oxide, these bodies at a temperature exceeding 180° C. gradually oxidise the india rubber, converting it into black carbonaceous masses, which might afterwards be taken to represent carbon black present in the mixing. This difficulty may be avoided in the case of the nitrobenzene treatment, by adding to the nitrobenzene $\frac{1}{10}$th or $\frac{1}{15}$th volume of chloroform, whereby the boiling point is reduced from 208° C. to about 170° C. A mixture of 100 parts of nitronaphthalene and 5 parts of chloroform also appears to act even better than nitro-naphthalene alone, but there is, of course, only an insignificant lowering of the boiling point in this case, and I prefer, therefore, to carry out the nitro-naphthalene treatment in an air bath which can without difficulty be kept at the safe temperature of 180° C.

The treatment named, applied to residue F, for the separation of the india rubber from the mineral matter is therefore carried out as follows:— The residue F, the weight of which is known, is placed in a weighed wide-

[1] This is especially the case if the mineral matter consists of Sb_2S_5, or of ZnO.

necked flask together with from 60 to 70 grms. of α-nitro-naphthalene, M.P. 58° C. The flask is then placed in an air bath, almost completely enclosing it. The air bath carries a thermometer, and care should be taken that the temperature is kept as near 180° C. as possible. The form and construction of this air bath is represented in figs. 24 and 25.

The cylindrical body (*a*) of the air bath is made of stout copper. It is provided with a covering of stout asbestos paper, or thin asbestos sheet. The bottom (*b*) of the bath should not be soldered to the body, but secured on the flanges *c* by means of screws, joints being made with asbestos.

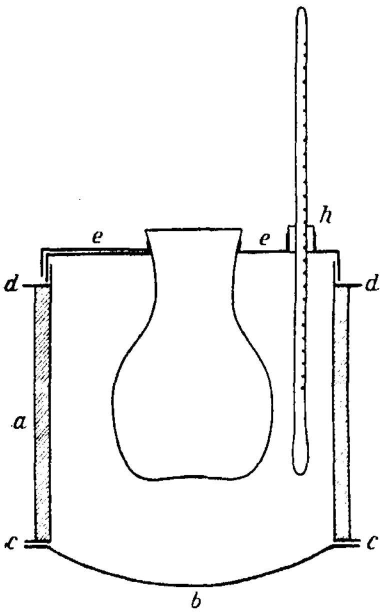

FIG. 24.—Diagram of air bath for nitro-naphthalene extraction.

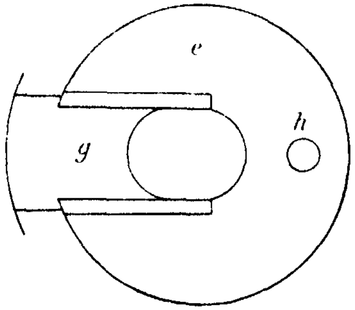

FIG. 25.—Diagram of air bath, construction of lid.

This avoids much trouble in repairs, as the bottom of the bath has to be frequently renewed. On the top the body has a collar *d* provided, over which fits the cap *e*. The latter is slotted in the manner shown in fig. 25, just wide enough to allow the neck of the flasks to pass. The flask being passed in the slot, it is secured in its position by the slide, and the grooves *g* in the edges of the two semicircular sections of the slot and the slide. Asbestos cording is fixed so as to secure a tight joint round the neck of the flask. The opening *h* is for the thermometer.[1] This is an extremely serviceable air bath. The desired temperature is reached very quickly, and as easily regulated. It may be mounted on tripod legs, or simply placed on a round tripod of suitable dimensions. To prevent too direct a radiation

[1] This air bath may be obtained from Messrs. Fred. Jackson & Co., 11 Half Moon Street, Manchester.

of heat from the bottom of the bath to the flask, I cover the former on the inside of the bath with a thin layer of fluffy asbestos fibre.

During treatment the contents of the flask are at frequent intervals gently stirred with a small glass rod. The completion of the solution requires from fifteen to sixty minutes according to the description of the sample. If the solution is completed, the flask is taken from the bath, allowed to cool, diluted with about 150 c.c. of benzene, and left to stand for the mineral matter to settle out. The solution is then filtered, flask and filter washed thoroughly with warm benzene, and subsequently dried for one hour at 110° C. We obtain in this manner the weight of the mineral matter, pigment colours, carbohydrates, and organic fibrous materials which may be present in the sample. The loss of weight is put down as india rubber, including sulphur of vulcanisation and chlorine in india rubber (chlorine of vulcanisation). The separation effected is therefore as follows:—

G.—Solution.	H.—Residue.
I. India Rubber, Gutta Percha, Balata. Dissolved but not determined. III. Sulphur of Vulcanisation. IV. Chlorine in India Rubber.	II. Carbohydrates. III. Sulphur in Inorganic Constituents. V. Inorganic Constituents. Fibrous Materials.

The india rubber cannot be recovered from its solution in the above filtrate, for the simple reason that it is no longer there in the form of india rubber, but of decomposition products of the latter. For this reason it is also impracticable to determine the sulphur of vulcanisation and the chlorine in the india rubber by means of this solution.

It is also impossible, therefore, to detect admixture of the rubber with gutta percha or Balata as soon as the india rubber is at all fully vulcanised. In only slightly vulcanised articles it is possible to extract the gutta percha and Balata by repeated treatment of the original sample with cold benzene, and precipitation of the benzene extract with absolute alcohol. It is, however, very rare that a sample of manufactured india rubber contains more than 1 or 2 per cent. of either gutta percha or Balata, and there is amongst india rubber technologists very considerable divergence of opinion respecting the practical value of these admixtures.

Much more serious is the fact that, as yet, we are practically unable to detect, with any degree of certainty, the admixture of 'recovered' india rubber; still less, of course, can we estimate its amount. Nor do the physical tests—in particular, the much vaunted tensile strength test—in the least assist us to arrive at any conclusion in this respect. This is all the more regrettable as 'recovered' india rubber is now very commonly used in goods in which its employment must appear in the highest degree injudicious. This applies notably to bicycle and carriage tires.

In an earlier chapter (III.) I have shown that all recovered india rubber, in spite of its trade description as 'devulcanised' india rubber, still contains the whole of the sulphur of vulcanisation of the waste rubber from which it has been obtained. I have further shown that all this recovered rubber again takes part in the vulcanisation of the article manufactured with its aid. Indeed, this is even true of the ground rubber waste (rubber dust), which is also largely used in the manufacture of rubber goods. This must not infrequently lead to an abnormally high coefficient of vulcanisation,[1] which may therefore occasionally serve as a criterion as to the proportion of recovered rubber present.

From the above it will be seen that there lies still a large unexplored field before us, and a great deal of patient research and experiment will be required before we shall be able to differentiate analytically the constituents of the rubber portion of a sample of manufactured india rubber.

The filter with the residue *h* upon it is replaced in a funnel, and washed with water heated to boiling in the flask in which the nitrobenzene treatment was carried out. Washing the filter with 150 to 200 c.c. of boiling water, added in small quantities at a time, is quite sufficient to remove from the residue all dextrine or soluble starch present. The filtrate is tested for the presence of dextrine or soluble starch by the iodine test.

If either of these two substances has been detected, filter and flask are again dried as before, and the loss of weight noted. This loss may represent either dextrine, or farina, or other starchy matter, which in the nitrobenzene treatment is partially converted into soluble starch, but chiefly into dextrine. To decide as to which form the carbohydrate is present in the rubber, some of the original sample is boiled with water for a few minutes. The water is then filtered off, and the filtrate tested for dextrine as above. According to the result of this test, the carbohydrate observed is put down either as dextrine or as farina.

The result of this determination leaves our analysis as follows:—

I.—Solution.	K.—Residue.
II. Carbohydrates. V. Inorganic Constituents (total).	III. Sulphur in Inorganic Constituents. IV. Inorganic Constituents (detail). **Not determined in solution G.** III. Sulphur of Vulcanisation. IV. Chlorine in India Rubber.

The items which have still to be determined are those appearing in the right column of the above table.

Before proceeding with the residue K, it should be closely examined for the presence of vegetable or animal fibres. If any are present, and the

[1] Respecting the significance of this term, the chapter following should be consulted.

determination of their amount is of importance, a fairly approximate separation from the mineral matter may be effected by shaking a weighed quantity of the residue with chloroform. This operation is best carried out by placing the residue in a test tube, pouring about 20 c.c. of chloroform upon it, very slightly shaking the tube, and allowing it to stand for some time, during which it is repeatedly tapped. The mineral matter settles at the bottom, while the vegetable and animal fibres rise to the top. They are floated off into a dish by holding the test tube in an inclined position and overflowing it with chloroform which is run in from a pipette, the outflow end of which is all the time kept in the chloroform in the test tube. The chloroform is evaporated from the dish, and the fibres remaining behind are transferred by the aid of a camel-hair brush to a watch-glass and weighed. From the weight of fibre thus found, the total amount of fibres present in residue K may be readily calculated.

If the residue K contains any carbon black, the presence of which is always easily recognisable, the only way to estimate it with a fair degree of approximation consists in burning off part of the residue K with lead chromate in the manner adopted for the elementary analysis of organic bodies containing sulphur.[1]

The detailed qualitative examination, followed by the quantitative estimation of the inorganic constituents of the mineral residue K, is, of course, conducted on the well-known lines of qualitative inorganic analysis, a description of which in this place is unnecessary. The variety of inorganic constituents to be found in manufactured india rubber is at times astonishing, often defying explanation. Nevertheless will it be found that in the large majority of cases a comparatively small number of inorganic compounds are used. A list of those compounds I have observed in a very large variety of rubber goods I give below. They are arranged approximately in the order of their technical importance and the frequency with which they occur.

Litharge, PbO.
Paris White, Whiting, $CaCO_3$.
Zinc White, ZnO.
Lime, CaO.
Barytes, $BaSO_4$.
Lithopone, $ZnS, BaSO_4$.
Golden Sulphide, Sb_2S_5.
Lamp Black, C (chiefly).
Magnesia, MgO.
Red Lead, Pb_3O_4.
Red Iron Oxide, Fe_2O_3.
French Chalk.
China Clay.
Vermilion, HgS.
Plaster of Paris, $CaSO_4$.
Gypsum, Pearl White, $CaSO_4$, 2 aq.
White Lead.
Infusorial Earth, Kieselguhr, SiO_2.
Zinc Sulphide, ZnS.
Lead Sulphide, PbS.
Lead Thiosulphate, PbS_2O_3.
Lead Sulphate, $PbSO_4$.
Graphite, C (chiefly).
Magnesium Carbonate, $MgCO_3$.
Pumice Stone Powder.
Glass Powder.
Mica.
Arsenious Sulphide, As_2S_3.
Zinc Dust.
Aluminium Powder.
Iron Filings.
Brass Filings.
Asbestos.

[1] If the residue contains graphite (plumbago), this would, of course, also be found as

It may safely be said that fully 80 per cent., probably even more, of the manufactured india rubbers are produced with one or more of the first twelve of the above named substances present, and these are also the ones which are the easiest identified. In respect of some of the others, identification in the purely chemical way is often extremely difficult—indeed, frequently the easiest and quickest way consists in a microscopic examination. Gypsum, as distinguished from plaster of Paris, infusorial earth, lead sulphate, pumice stone, glass, mica, and asbestos, can readily be identified in this manner, and it is advisable to have a set of slides of all these products, simply mounted in air, always ready for comparison. In doubtful cases examination in polarised light often proves useful.

For the quantitative determination of the inorganic compounds, the simplest way frequently is to dissolve a fresh part of the sample in nitric acid, evaporate to dryness, add a few drops of strong sulphuric acid, drive off the excess on the sand bath, and proceed with the residue in the well-known manner. But, if it is preferred, some of the original sample may, after extraction with acetone, be immediately subjected to the nitrobenzene treatment, and the quantitative determination of the mineral constituents completed by the analysis of the residue obtained. This course is particularly to be recommended with samples yielding easily to the nitrobenzene treatment.

The determination of the sulphur in the inorganic constituents is carried out by placing a small incineration dish of about 6 cm. diameter upon the water bath, charging it with about 10 c.c. of fuming nitric acid, and adding a weighed quantity of the residue K in small portions. It is advisable during this operation to keep the dish covered with a watch-glass to avoid loss through spirting. After the whole of the substance has been added, the watch-glass is thoroughly wiped with moistened filter-paper cuttings, which are then also added to the acid. The whole is then evaporated to a syrupy consistency, when about 2 grms. of pure sodium acetate are added, and the whole evaporated to dryness. The dry mass is carefully ignited over a Bunsen burner, the carbonaceous matter oxidised by cautiously adding potassium nitrate, preferably in the form of small crystals. The whole is then kept in quiet fusion for a short time, the dish allowed to cool, the melt dissolved in boiling water, filtered, and the filter thoroughly washed with hot water. The filtrate is then acidulated with hydrochloric acid, heated to boiling, the sulphuric acid precipitated with a hot solution of barium chloride, and the weight of the barium sulphate obtained ascertained in the usual manner. The amount of sulphur thus found is, of course, in the first instance calculated upon the total mineral matter ascertained in the sample; its percentage, however, being calculated upon the whole of the rubber sample.

We now determine the total sulphur in the sample by weighing out from 1·5 to 2 grms. of the original sample, and adding this quantity in small portions to about 15 c.c. of nitric acid (about 64 per cent. strong,

not 'fuming') contained in an incincerating dish of the already named description. The dish is placed on a water bath and covered with a watch-glass, the whole operation being carried out exactly in the manner already described for the determination of the sulphur in the mineral matter.

We now have determined the following forms of sulphur in the rubber sample:—

1. Free sulphur.
2. Sulphur in pitch, tar, and bituminous bodies.
3. Sulphur in fatty substitutes.
4. Sulphur in inorganic compounds.
5. Total sulphur in sample.

It is therefore obvious that by adding the amounts of sulphur of the first four determinations, and deducting the sum from the total sulphur, the difference of the latter over the former must represent the sulphur in combination with the india rubber—in other words, the sulphur of vulcanisation.

It might, however, be objected, and not unjustly, that considering the great importance of the sulphur of vulcanisation, its determination by calculation from possibly five separate determinations, the errors of which under unfavourable conditions would all accumulate in this final calculation, would tend to render the result of doubtful value. For this reason it is much more satisfactory to treat from 1 to 1·5 grms. of the original sample, according to its now ascertained components, with the above mentioned extraction solvents, so as to reproduce a residue K,[1] the total sulphur of which is ascertained exactly as the total sulphur in the sample. By deducting from the figure thus obtained the sulphur contained in the mineral matter, we obtain at once the sulphur of vulcanisation.

There remains now only the determination of the chlorine in the india rubber, which is carried out as follows. About 0·3 grm. of the rubber sample[2] are sealed up in a bomb tube with 5 c.c. of fuming nitric acid and 1 grm. of silver nitrate.[3] It is generally advisable to heat the tube for two days in the 'bomb' furnace, relieving it, of course, of its pressure by unsealing the capillary, and re-sealing it, as soon as the gases have escaped, prior to resuming the heating on the second day. When the cold tube is opened and cut, its contents are washed with hot water into a small glass beaker, and the precipitate filtered off. If the india rubber sample contains no mineral matter insoluble in nitric acid, the washed filter residue consists simply of silver chloride, the weight of which is ascertained in the usual manner. But in most cases other insoluble matter is present. In this case the filter residue is washed neutral and dried. It is then placed in a porcelain crucible, the filter burned, and its ash added to the precipitate.

[1] This to remove the free sulphur present, which may greatly retard the completion of the nitrobenzene treatment.

[2] If the sample contains chlorosulphide substitutes, extraction with alcoholic caustic potash must precede the above determination.

[3] For particulars consult GATTERMANN, *Practical Methods of Organic Chemistry*.

The whole is then carefully mixed with from 6 to 10 times of its weight of sodium carbonate, and the mixture fused over a powerful Bunsen burner. The fused mass is dissolved in water, filtered, and the filter residue thoroughly washed. The latter is then washed off the filter into a porcelain dish, the filter washed with about 50 c.c. of hot 5 per cent. strong nitric acid, which is allowed to run from the filter into the basin. The contents of the latter are then heated for about ten minutes to near boiling point, the solution then filtered, and the filter residue carefully washed neutral. To the filtrate, the total volume of which should not exceed 100 c.c., hydrochloric acid is added in very slight excess, the precipitated silver chloride filtered off and treated in the usual manner for weighing. We obtain in this manner the amount of chlorine contained in the rubber of the sample.

The whole of the analytical data obtainable, and the successive processes by which they are obtained, are embodied in the following table:—

I. EXTRACTION WITH ACETONE.						VI. SEPARATE ESTIMATIONS.
A.—SOLUTION.	B.—RESIDUE. II. EXTRACTION WITH PYRIDINE.					Total sulphur. Chlorine in rubber.
Resinous constituents of india rubber. Fatty oils. Mineral oils. Resin oils. Solid hydrocarbons. Resins. Free sulphur.	C.—EXTRACT.	D.—RESIDUE. III. EXTRACTION WITH ALCOHOLIC POTASH.				
	Tar. Pitch. Bituminous bodies. Sulphur in above.	E.—EXTRACT.	F.—RESIDUE. IV. EXTRACTION WITH NITRO-NAPHTHALENE.			
		Chlorosulphide substitutes. Sulphide substitutes. Oxidised (blown) oils. Sulphur in substitutes. Chlorine in substitutes.	G.—EXTRACT.	H.—RESIDUE. V. EXTRACTION WITH BOILING WATER.		
			India rubber. Sulphur in india rubber. Chlorine in india rubber. The total of above three estimated by loss.	I.-EXTRACT.	K.—RESIDUE.	
				Starch (Farina). Dextrine.	Mineral matter. Free carbon, fibrous materials. Sulphur in inorganic compounds.	

The number and nature of the analytical operations required for the complete analysis of an india rubber sample may appear alarming to many, but it may be at once pointed out that the number of individual determinations recorded in the above scheme are probably never required in the analysis of any one sample. Indeed, in many cases a complete analysis is not required at all, one or two of the above operations furnishing all the information required. It must therefore be decided from case to case which are the analytical data required to furnish any particular information asked for in respect of a certain sample. Not only is it, then, often

possible to abbreviate the above course, but also to substitute more expeditious, if somewhat less accurate, working methods in the place of those we have been recommending.[1]

The most usual shortening of the above scheme is rendered possible in the analysis of samples, the mineral matter of which contains neither sulphides, nor sulphates, nor any other sulphur compounds, and the detailed composition of which is a matter of secondary importance. If, moreover, the rubber sample is of the 'grey' or 'red' variety, the analytical course may be further shortened, as none of these rubbers ever contain any substances of the group C. of our above scheme. The mode of procedure then assumes the following comparatively simple form :—

<table>
<tr><th colspan="3">I. Extraction with Acetone.</th><th>Separate Estimations.</th></tr>
<tr><td rowspan="2">A.—Extract.
Resinous constituents of india rubber.
Fatty oils.
Mineral oils.
Resin oils.
Solid hydrocarbons.
Resins.
Free sulphur.</td><td colspan="2">B.—Residue.
III. Extraction with Alcoholic Potash</td><td rowspan="2">Mineral matter by ignition.
India rubber by difference.</td></tr>
<tr><td>E.—Extract.
Chlorosulphide substitutes.
Sulphide substitutes.
Oxidised (blown) oils.
Sulphur in substitutes.
Chlorine in substitutes.</td><td>F.—Residue.
S in rubber.
(Sulphur of Vulcanisation.)
Cl in rubber.</td></tr>
</table>

It will be seen that, in working according to this scheme, the extraction with acetone and the treatment with alcoholic potash have remained, and extracts A. and E. are therefore identical with the corresponding extracts in the preceding table. Residue F. is, however, here used for the determination of the 'sulphur of vulcanisation' and of the chlorine.

The estimation of the sulphur in residue F. is, of course, carried out in exactly the same manner as the determination of the total sulphur. The chlorine in this residue is determined by Carius' method, as already described. A rather quicker, although not quite so accurate method consists in mixing the rubber intimately with a fusion mixture consisting of 2 parts of sodium carbonate and 1 part of potassium nitrate, spreading this mixture evenly on the bottom of a platinum dish which has previously been covered with a thin layer of the same fusion mixture, and finally covering the rubber particles completely with the same. The mass in the dish is then very gently and gradually ignited. When the mass no longer gives off vapours, the heat is increased until the whole is in quiet fusion

[1] There is, of course, no necessity for a re-estimation of the respective extracts.

and all carbonaceous matter burned off. The fused mass, after cooling, is dissolved in water, filtered, the filter washed neutral, the filtrate acidulated with nitric acid, and the chlorine precipitated with silver nitrate. This operation should be performed in an ERLENMEYER flask, and not in a dish or beaker, in order to avoid loss through the effervescence taking place on acidulating the solution.

This same method has also been recommended for the determination of the total sulphur in the india rubber, but it is quite worthless for this purpose, the results obtained being much too low, often by over 50 per cent. of their actual value. The cause of this is obvious, and may easily be discovered by subjecting vulcanised india rubber to dry distillation, when it will be found that almost exactly one half of the sulphur present is given off in the shape of hydrogen sulphide, the rest in the form of organic sulphides. The former, no doubt, is readily oxidised by the fusing nitrate, but the greater part of the latter most probably are volatilised before any action takes place. The chlorine of the india rubber, on the other hand, is very readily given off at comparatively low temperatures, and it is, moreover, evolved entirely as hydrochloric acid, which is rapidly and completely absorbed by the sodium carbonate present.

In the above abbreviated scheme we determine the mineral matter by ignition. As is well known, this method is by no means accurate—indeed, if not very carefully carried out, it may be very faulty. From 1 to 2 grms. of the india rubber are thinly spread out in a weighed porcelain dish of about 6 cm. diameter. The latter is then heated over a small flame, so regulated that the vapours evolved never burst into flame : should this occur, it is a sign that the flame of the burner is too high. If the evolution of vapours has ceased, the flame is moderately increased until all the carbonaceous matter is burned off. The results are almost invariably too high, owing to part of the organic sulphur being retained either as sulphide in the presence of zinc oxide, or as sulphate in the presence of lime, magnesia, or litharge. The error thus incurred may amount to as much as 2 per cent., but the fact is that as far as the figures affected by it are concerned—mineral matter and india rubber—this fault is, in the majority of cases, of little, if any, practical account.

(c) NOTES ON THE ANALYSIS OF HARD RUBBER GOODS (EBONITE).

The analysis of hard india rubber goods suffers from even greater disadvantages than that of soft goods, as the india rubber constituent, which, in the former, only dissolves with difficulty, is, in the latter, totally insoluble. We have already incidentally alluded to the fact that the readiness with which a sample of soft rubber is resolved in the nitrobenzene treatment depends very materially upon the degree of vulcanisation—*i.e.*, coefficient of vulcanisation—of the sample, and decreases as the latter increases. Long before we reach products of a coefficient of vulcanisation as high as that of the typical hard rubbers, we arrive at products which

are irresolvable by any known solvent. This fact adds, of course, very considerably to the difficulty of the analysis of hard rubber goods. Some compensation arises, however, from the fact that hard rubber never contains any of the fatty substitutes. The organic non-rubber constituents of hard rubber consist entirely of resins and pitches. The inorganic constituents of hard rubber are much the same as those of soft rubber, but in smaller variety.

The preparation of a sample for analysis is again a point of importance. The only satisfactory way consists in reducing the sample, or as large a part of it as possible, to a fairly fine powder by means of a file. This powder is passed through a sieve of from 80 to 100 mesh per square inch. What does not pass through the sieve is ground in a well-adjusted grinding mill until the whole of the filings have passed the sieve; and after the fine powder thus obtained has been thoroughly mixed in a mortar, it may be taken to represent a fair average sample.

In analysing hard rubber, an estimation of the following constituents is desired:—

(*a*) India rubber.
(*b*) Resins, or resinous matters.
(*c*) Bituminous bodies, pitches.
(*d*) Mineral matter.
(*e*) Total sulphur, { Sulphur of vulcanisation. Free sulphur. Sulphur in mineral matter.

The analytical course to be followed may now be easily arrived at from the scheme given on page 255. It is as follows:—

<table>
<tr><td colspan="4">I. EXTRACTION WITH ACETONE.</td><td rowspan="4">IV. SEPARATE ESTIMATIONS.
Mineral matter.
Sulphur in mineral matter.</td></tr>
<tr><td rowspan="3">A.—EXTRACT.
India rubber resins.
Added resinous bodies.
Free sulphur.</td><td colspan="3">B.—RESIDUE.
II. EXTRACTION WITH EPICHLORHYDRINE.</td></tr>
<tr><td rowspan="2">C.—EXTRACT.
All resins insoluble in acetone.
Sulphur in above.</td><td colspan="2">D.—RESIDUE.
III. EXTRACTION WITH PYRIDINE.</td></tr>
<tr><td>E.—EXTRACT.
Bituminous bodies.
Pitches.
Sulphur in above.</td><td>F.—RESIDUE.
Sulphur in residue.</td></tr>
</table>

The extraction with acetone requires much more time in the case of hard rubber than with soft rubber goods—indeed, nothing less than a two days' extraction will be found satisfactory. This appears to be due to the fact that hard rubber contains the free sulphur in a peculiarly in-

soluble form—probably in an amorphous variety which only gradually passes into solution. This seems to be the reason why the substitution of carbon bisulphide[1] for acetone in this process proves no more expeditious, as the solubility of amorphous sulphur very largely depends on the temperature, and would therefore take place much less rapidly at the boiling point of carbon bisulphide (46° C.) than at that of acetone (56° C.), although the latter is a much inferior solvent for sulphur than the former.

The general conditions for carrying out the acetone extraction of hard rubber are exactly the same as that for soft rubber—that is, the powder of hard rubber, about 2 grms., is placed in an extraction thimble and treated for two days in the apparatus figured upon page 240 of this book.

As a rule, the organic extract obtained in this manner is very small in quantity, consisting chiefly of sulphur, the exact amount of which is ascertained by oxidation with fuming nitric acid, and determination of the sulphuric acid in the usual way.

If the amount of organic matter present, as ascertained by the difference between the amount of the total extract and the amount of free sulphur, exceeds 4 per cent., it may be assumed that resinous bodies or resins other than those naturally occurring in india rubber are present. A great number of the resins are soluble in acetone, others partially soluble, but these solubilities may undergo considerable changes in the course of the action upon them of high temperatures in the presence of a large amount of sulphur. For this reason the examination of the extracted resins can only deal with their general features, and the identification of any particular resin is always a matter of very great difficulty and uncertainty, especially as the chemistry of the resins is still in almost as chaotic a state as the chemistry of india rubber.

While acetone dissolves a considerable number of resins completely, it dissolves a number of them only partially, and others not at all, as will be seen from the following table, which contains those more generally used in india rubber goods, especially in the manufacture of hard rubber.

Name of Resin.	Acetone.	Epichlorhydrine or Dichlorhydrine.
Acaroïd Resin, ...	soluble.	soluble.
Amber, ...	insoluble.	,,
Gum Benzöin, ...	soluble.	,,
Colophony (Rosin), ...	,,	,,
Copal, ...	partially soluble.	,,
Dammar, ...	,,	,,
Elemi, ...	soluble.	,,
Gum Mastic, ...	partially soluble.	,,
Sandarac, ...	soluble.	partially soluble.
Shellac, ...	insoluble.	soluble.

[1] Owing to the almost imperceptible swelling action of carbon bisulphide upon hard rubber, the employment of this solvent in the extraction in place of acetone would otherwise be wholly unobjectionable.

From this table it is evident that in a number of cases the acetone extraction fails to remove the whole, and in two rather important instances to remove even part, of the resins present. We require, therefore, a further treatment with a solvent capable of extracting those resins which are insoluble in acetone.

Such a solvent we possess in epichlorhydrine, [1]and therefore the acetone extraction is immediately followed by extraction with this solvent. For this purpose it is quite unnecessary to dry the extraction thimble after the acetone extraction. As soon as the flask containing the acetone extract is taken off, a similar weighed flask containing about 75 c.c. of epichlorhydrine is connected with the extractor. Owing, however, to the higher boiling point of epichlorhydrine (117° C.), this flask must now be heated upon the sand bath, or upon an asbestos-coated piece of wire netting. Three hours' extraction fully suffice to remove all the residual resins present. The flask is then removed, and the epichlorhydrine distilled off. To avoid overheating and decomposition of the resins extracted, the flask is heated in a paraffin bath, the temperature of which is kept at from 120 to 122° C. Finally, the flask is dried for two hours at 110° C. after its outside has been carefully cleaned by wiping it first with filter paper, and then with filter paper moistened with benzene.

This extract not infrequently contains sulphur in organic combination, the amount of which may readily be estimated in the same manner as the sulphur in extract C. (*see* page 244).

In proceeding next to the extraction with pyridine, it is advisable first to dry the paper thimble and its contents, as pyridine and epichlorhydrine interact with each other. The dry thimble is then replaced in the extractor, to which a weighed flask containing about 60 c.c. of pyridine (B.P. 109 to 111° C.) is fitted. It is heated upon a sand bath or in an oil bath, the temperature of which is kept at from 116 to 120° C. Extraction being complete, which is easily judged by the extraction thimble having resumed its normal colour, the flask is taken off and the pyridine distilled off in an oil bath at a temperature not exceeding 120° C. The flask is then carefully cleaned and dried until the smell of pyridine has completely disappeared, when the weight of the extract may be ascertained.

Also in this extract the sulphur should be determined whenever a fully detailed analysis is required. The determination of the sulphur is carried out in the manner described on page 244.

In the residue from the extraction with pyridine we determine the sulphur present in the same manner as the 'total sulphur in rubber' is determined. The amount of sulphur thus found represents the sum of the sulphur of vulcanisation and of the sulphur in the mineral matter. In order to ascertain the sulphur of vulcanisation, we must therefore estimate the sulphur contained in the mineral matter in the form of sulphides and sulphates.

[1] Dichlorhydrine is not so suitable on account of its high boiling point (177° C.).

To this end we first determine the mineral matter in the sample by incinerating a weighed quantity and making a complete analysis of the ash in respect of the bases present. All the lead found is calculated as litharge, the antimony as the pentasulphide, and the mercury as mercuric sulphide. Any zinc found may be present either as oxide or sulphide; calcium may be present either as carbonate or sulphate[1]; barium is present either as carbonate, but much more frequently as sulphate; magnesium is always present as oxide. Information upon this point is obtained by treating a sample of the ebonite powder with warm hydrochloric acid (1 : 3). Any hydrogen sulphide evolved will be due to the presence of zinc sulphide, evolution of carbonic acid to calcium carbonate. If no barium passes into solution, this may be taken to prove that any present is in the form of barium sulphate.

According to the results thus obtained, the quantities of sulphur corresponding to the amount of zinc present, calculated as zinc sulphide, and of the amount of barium present, calculated as barium sulphide, together with any sulphur present in the form of antimony pentasulphide and mercuric sulphide, are deducted from the amount of sulphur determined in the residue F., and the difference taken as sulphur of vulcanisation. It is scarcely necessary to point out that in every case the respective percentages must be calculated upon the whole of the sample from which the residue F. is derived.

It could not be said that this method for the determination of the sulphur of vulcanisation in hard rubber is particularly accurate. Tangible errors must be caused if zinc or barium should be present in two forms at the same time. That this ever occurs in respect of barium is highly improbable, but is perhaps not so very uncommon in respect to zinc, as, for instance, the use of both zinc oxide and lithopone (ZnS, $BaSO_4$) in the same mixing has several points of practical import to recommend it.

By way of a further, but by no means very accurate, control of the amount of mineral matter present, a sample of the hard rubber is incinerated with the same precautions as are observed in the case of soft rubber. The loss of weight is, of course, organic matter, together with the whole of the sulphur not present in inorganic combination. In the interest of further control of the total of the sulphur determinations, a determination of the total sulphur in the original sample is also desirable.

We have thus estimated :—

1. **Extract from acetone.**
2. **Extract from epichlorhydrine.**
3. **Extract from pyridine.**
4. **Total sulphur,**
   - (a) Sulphur in 1.
   - (b) Sulphur in 2.
   - (c) Sulphur in 3.
   - (4) Sulphur in residue from pyridine.
   - (5) Sulphur in mineral matter.
5. **Mineral matter.**

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[1] Quite negligible amounts also as hydroxide.

The difference between all these determinations, expressed in percentages from 100, represents the percentages of india rubber present in the sample. Like all indirect estimations, this is also open to a number of objections and errors. With normal samples these are hardly serious, but in exceptional cases they may become rather troublesome. This simply amounts to saying that there are more limitations to our present power of analytical discrimination of the organic constituents of hard rubber goods than in the case of soft rubber goods. Imperfect as are these analytical methods at the present moment, they are, however, already a valuable aid in gaining an insight, otherwise unobtainable, into the rationale of many of the crudely empirical processes of the india rubber factory, and in throwing light upon an ever-increasing number of the many obscure phenomena observed, as well as on the behaviour, in practical work, of manufactured india rubber. Considering the years of work required to bring the analysis of many infinitely less refractory industrial products to a satisfactory conclusion, the results at present obtainable in rubber analysis are highly gratifying, but it is neither a very suitable field for the half-educated chemist, nor for the chemist who merely wants 'to do rubber,' to engage in.

(*d*) Interpretation of Analytical Results.

Once the analytical figures have been obtained, we have to interpret them. This may be a very simple operation, according to the question the analysis is intended to solve; or it may be a task of extreme difficulty, one at any rate involving a thorough acquaintance with every known point of the chemistry of india rubber, as well as extensive practical experience in its manufacture. It is an utter impossibility to discuss exhaustively the interpretation to be placed upon every one of the available analytical data, or every combination of them, so as to embrace every possible case; but there are, with regard to every one of these data, certain features of permanent significance, and these I now propose to discuss in the order in which they appear in the various consecutive operations of the analytical scheme above set out.

1. **Extraction with Acetone.**—To the extraction with acetone I attach considerable importance. It gives us, at the very outset, a very fair idea, both from the point of view of its quantity and of its quality, of the general character of the sample under examination.

A sample consisting only of india rubber and sulphur, or india rubber, sulphur, and mineral matter, always yields a very clean-looking extract, whatever kind of india rubber it contains. The extracts in this case are rather light in colour, and do not prevent the separation of the sulphur in well-formed crystals. By washing such extracts about five times in succession, each time with 2 c.c. of acetone in the cold, and filtering the successive washings into a weighed flask through a very small filter, a very satisfactory separation of the organic extract, due to india rubber, from the

free sulphur present may be effected. In doubtful cases it is not quite easy to decide whether the sulphur is actually free from all organic impurities. A good test in this case is to add to the sulphur residue in the flask about 2 c.c. of carbon bisulphide, this preferably filtered through the filter which served for the acetone washings. The sulphur almost instantly dissolves, and the carbon bisulphide is now evaporated on the water bath, and the flask then for a few minutes dried in a water oven. In the absence of all organic matter the sulphur in the flask is thus obtained in the form of globular masses of liquid (colloidal) sulphur adhering to the sides. These globules often persist for days without crystallising. In the presence of mere traces, even of organic matter, these globules are not obtained, the sulphur at once forming somewhat indistinctly crystalline scales on the sides of the glass.

The amount of organic extract obtained from rubber samples as above described depends, of course, entirely upon the brand of india rubber used in their manufacture, and for this reason the organic extract obtained from such samples enables us to draw a general conclusion of the class of rubber used for their manufacture, though not of the particular brand. This, even with the limitation stated, is always a valuable point in rubber analysis. Now, from the table given on page 3 of the first section of this book, it appears that the percentage of resinous extract yielded by the fine grades of Pará rubber is very regular indeed, amounting almost uniformly to 1·3 per cent., but from this it must not be assumed that a sample of manufactured Pará must, on analysis, yield no more than 1·3 per cent. of organic extract. It is a common property of all kinds of rubber to show a considerable increase of resinous matter after vulcanisation. But in order to recognise the relation of the resinous extract obtained to the amount of india rubber present, the percentage figures for these two constituents must always be calculated separately, so as to show the absolute percentage of resin contained in the india rubber of the sample alone. Thus, a sample[1] might have yielded the following figures on analysis :—

India rubber,	24·49	per cent.
Organic extract,	1·10	,,
Free sulphur,	1·23	,,
Sulphur of vulcanisation,	0·84	,,
Mineral matter,	72·33	,,

At first sight the amount of organic extract found might appear to be well within the limits of the figure to be expected for pure Pará, but very little reflection will show that the percentage of organic extract is stated here in relation to the whole mixing instead of in relation to the amount of india rubber alone. For this reason it is advisable to append to the percentage figures of every analysis a synoptical figure—organic extract in india rubber—stating the percentage of this constituent in the india rubber itself. In this way we obtain for the 'organic extract in india

[1] The sample was a roller covering manufactured from fine Pará.

rubber' the figure 4·29.[1] This curious increase of the 'resinous' matter of india rubber in the course of vulcanisation, which I have already remarked upon in an earlier paper,[2] not only occurs in Pará rubber, but in all brands of india rubber generally, and it amounts in all cases I have examined to an increase of from 3 to 5 per cent. The following table contains the figures of a few typical varieties of india rubber after vulcanisation with 10 per cent. of sulphur :—

Brand of Rubber.	Resin in Washed Rubber.	Resin in Vulcanised Rubber.
Pará, fine, ...	1·2 per cent.	4·04 per cent.
Ceara, ...	2·1 ,,	5·12 ,,
Upper Congo, ...	3·7 ,,	7·60 ,,
Lagos, ...	4·5 ,,	7·13 ,,
Sierra Leone, ...	6·1 ,,	9·97 ,,
Borneo, ...	10·3 ,,	14·44 ,,

This fact discounts to a considerable extent the value of the conclusions drawn in respect of the india rubber contained in an unknown sample upon the basis of the resinous extract obtained. On the other hand, however, on what is always the most important question in this relation —namely, whether any one sample has been manufactured from Pará —the percentage of resinous extract obtained may always be used as a very safe guide. The highest percentage of extract I ever obtained from vulcanised Pará never reached 4·5 per cent., and always exceeded 3 per cent.

Of course this increase in the resinous extract only occurs in warm vulcanised rubber; cold vulcanised samples invariably show the normal percentages of resinous matter. The above mentioned increase is, as I have satisfied myself by special experiments, chiefly due to the heating of the rubber, and in a lesser degree to the action of the sulphur, probably upon the oxygenated bodies which are contained in the crude india rubber, and which are considerably larger in amount than the resins which can be extracted from it by means of acetone.

India rubber goods which have undergone oxidation always show a

[1] It is obvious that this figure is not strictly accurate. The technically pure india rubber, from which the above article was manufactured, contains the resinous matter subsequently extracted as a natural constituent. The proper course would be, therefore, to add the percentages of rubber and resin found, and calculate the percentage of resin observed upon this sum. But this would lead to considerable errors in the case of samples yielding large percentages of organic extract due in small part only to the rubber present, but chiefly derived from free oils, fatty substitutes, and the like contained in the sample. It is therefore all round preferable to calculate, as we have done above, the ratio between the percentage of actual rubber and the percentage of organic extract observed. The error thus introduced is smaller than the variations in the percentage of resin in crude india rubber.

[2] "On the Analysis of India Rubber Articles," *Journ. Soc. Chem. Ind.*,' 1894, pp. 3650–3658.

more or less considerable increase of the resinous extract, and by the time a sample has suffered from oxidation to such a degree as to render it clearly defective, it will show an amount of resinous matter very largely in excess of the normally occurring amounts.

The presence of mineral oils is always clearly recognisable by the strong colour, and particularly by the characteristic fluorescence, they impart to the acetone solution. They are easily separated from the resinous constituents of the extract by means of absolute alcohol, in which they are quite insoluble. In fact, this is a very satisfactory method for their separation and estimation.

Not infrequently the organic extract contains resin oils instead of mineral oils. Their presence generally betrays itself by the blue fluorescence of the acetone solution. They may be more definitely identified by their very characteristic odour, and still better by RENARD's reaction with anhydrous stannic chloride, with which they develop a very fine and intense purple coloration.[1]

Mineral or resin oils are frequently added to india rubber mixings. They also form one of the constant constituents of recovered rubber. As soon, therefore, as the presence of any of these oils is observed, this point should be remembered, as, in conjunction with other criteria to be mentioned later, it often enables us to pronounce upon the presence of recovered rubber in a sample under examination.

Free fatty oils in the extract occur just as often as mineral oils. Either they have been added as such to the mixing—tallow being also occasionally used in this manner—or they are derived from fatty substitutes present which contain from 2 to 14 per cent. of soluble glycerides. Of course it is also possible that substitutes and free fatty oils are at the same time added to a rubber mixing.

The insolubility of these oils renders their separation from the resinous extract a very simple matter. It is effected by repeated treatment with absolute alcohol, in which the fatty oils, with the exception of castor oil, are practically insoluble.

If in these fatty oils the presence of mineral oils is suspected, they should be saponified with a few cubic centimetres of alcoholic caustic soda. This solution is evaporated to dryness, the residue taken up with boiling water, transferred to a small separating funnel, and extracted with ether. On evaporating the ether, any mineral oil present remains behind and may be further identified.

If no fatty substitutes are present, any oils found in the extract must have been added to the rubber mixing either as such or in the form of recovered rubber, which very uniformly contains about 8 per cent. of them.

[1] ALLEN recommends in place of stannic chloride the use of stannic bromide, which is easily prepared by dehydrating bromine with sulphuric monohydrate in a small separating funnel, and allowing it to flow, drop by drop, upon tin shavings contained in a well-cooled flask.

If fatty oils alone are present, the inference is obvious: in the presence of fatty substitutes, at least part of them will be derived from these. If the amount of fatty oils present does not exceed 10 per cent. of the amount of fatty substitutes, the addition of free oils as such to the rubber is very improbable.

It not infrequently happens that the correctness of an analysis is challenged if mineral oils or fatty oils are reported as present. This, of course, can only happen if the sample in question contains recovered rubber or fatty substitutes respectively, of the composition of which most rubber manufacturers are blissfully ignorant. It is therefore advisable, in preparing a report, always to point out that mineral oil, if any be present, may or may not have been added as such. Similarly, attention should always be called to the relation of fatty oils to fatty substitutes.

For manufacturing purposes it is comparatively irrelevant whether any fatty oil found in a sample to be matched has been added as such, or whether it is derived from the fatty substitutes present, but it is, of course, necessary to ascertain the percentage of free fatty oil in the substitutes which are to be employed, and to make up the deficiency of free fatty oil, so as to bring it to the proportion of the free oil in the sample. If the total of free fatty oil in the substitute is, however, more than the corresponding proportion in the sample, it is obvious that a substitute containing less free oil should be employed.

The same principle must also be observed in respect of the amount of resinous extract ascertained in the sample, and it is obvious that the amount of resin contained in the rubber to be employed must be taken into consideration.

Whether any mineral oil present has been added as such in the manufacture of the sample, or whether it is due to the presence of recovered rubber, is a question which at present cannot be decided by chemical means. Often the tensile strength test furnishes indications on this point.

The presence of paraffin wax or ozokerite, of which some samples contain as much as 15 per cent., always betrays itself by the peculiar waxy character of the extract, and also by its comparative insolubility in cold acetone. Not infrequently these hydrocarbons are added to the mixing in the form of a preparation which is now in the market under the name of 'Nantusi,' but which for a number of years has been employed by several firms with a great display of secrecy. It is a quack 'medicine' against suncracking, consisting of about 30 per cent. of sulphur and about 70 per cent. of a mixture of paraffin wax with a small quantity of bee's-wax and tallow. If it is desired to determine quantitatively the amount of paraffin wax or ozokerite present, the extraction residue is warmed with about fifty times its weight of glacial acetic acid. All the resinous and fatty extract, together with mineral oils present, is dissolved. The paraffin wax, on cooling, separates out almost quantitatively, 1 part

of it requiring 1668 parts of acetic acid for solution.[1] The solution is filtered off through a small filter, flask and filter are washed with a little acetic acid, the filter placed upon the flask containing the paraffin wax, and any particles of the latter which are upon the filter washed back with about 50 c.c. of warm carbon bisulphide. The latter is then distilled off, and the flask dried and weighed.

Incidentally it may be of interest to remark upon the effect of paraffin wax in rubber mixings. It lies, briefly, in the fact that india rubber and paraffin wax will not intermix homogeneously to form a sort of colloidal solution. Indeed, india rubber is quite insoluble in paraffin, and therefore does not absorb it as it absorbs a solvent. As the result of this, there is a distinct tendency in compounding india rubber and paraffin wax for the latter to be squeezed out of the mixing. This is, indeed, what happens if an excess of paraffin wax is used. What represents an excessive proportion depends, however, largely upon the other constituents and their proportions in the mixing. Now, under the influence of the heating of the mixing upon the rollers, the paraffin wax melts, and by capillary action fills the pores of the mixing, thereby greatly reducing the absorptive power of the manufactured india rubber for water and oxygen. The effect of this is, of course, to correspondingly reduce the liability of such india rubber to oxidation in general, and to suncracking in particular, which, as I have already pointed out, is simply oxidation accelerated by the influence of the actinic rays of the sun. There is, however, this disadvantage, that this immunity against oxidation is obtained at the expense of tensile strength. This result, which any physicist might at once predict for a mixture of two bodies of the nature of paraffin wax and india rubber intermingled, is in some cases quite immaterial, although objectionable in the highest degree in others. In bicycle tyres, I have, in a large number of cases, observed a reduction of tensile strength amounting to more than 50 per cent. Under the most favourable conditions of manufacture, this may be reduced to about 30 per cent., which is still quite prohibitive in an article requiring to withstand so much wear and tear.

II. **Extraction with Pyridine.**—Additions of tar—both coal tar and that obtained in the destructive distillation of wood (Stockholm tar)—and pitch are frequently made to rubber mixings. Their action consists in the facilitating of the mixing operation, and also in the reduction of the porosity of the manufactured india rubber. Asphaltum is also occasionally used for this purpose, but its advantage is not very apparent.

The tar is often added in its crude commercial state, but more frequently the plan is adopted of thickening it by continued heating, generally with addition of resin, until it forms, when cold, a scarcely tacky, semi-elastic, but not brittle, mass. In using asphaltum, no such operation is required, as the asphaltum of commerce already forms a hard, very brittle body, which can easily be powdered. According to Henriques, asphaltum

[1] Pawlewski and Filemonowicz, *Ber.*, xxi. p. 2973.

is much used in large proportions in india rubber mixings; but as far as the author's experience goes, it tends to show that, at any rate in soft rubber goods, its use is of the rarest occurrence. It may possibly find a somewhat more extensive employment in hard rubber goods, but its advantage in such mixings over many other organic 'filling agents' is by no means clear.

It is in most cases impossible to decide whether crude or boiled tar has been added to a sample, but it is safe to assume, in the absence of contrary evidence, that in 'spread' goods the former, and in moulded, calendered, or 'built up' goods the latter, has been employed.

Not infrequently coal tar contains a considerable amount of carbonaceous matter which, of course, is not extracted by the pyridine. This carbonaceous matter is encountered in the subsequent estimations, and there is no possibility of distinguishing it from lamp black, which may, or may not, be present at the same time. Of this carbonaceous matter crude gas tar contains generally about 15 per cent., but as much as 35 per cent. have been found occasionally. Boiled tar contains about 20 per cent. of it. Considering that the proportion of tar added to rubber mixing varies in the vast majority of cases from 0·5 to 1 per cent. of the total mixing, and only in quite exceptional cases amounts to 2 per cent., it is evident that the possible error due to this carbonaceous matter is so small that it is without any sensible influence upon our determinations.

Incidentally it may be mentioned here that it is sometimes desirable, for manufacturing purposes, to know the amount of carbonaceous matter contained in either crude coal tar, or in the boiled tar, or in coal tar pitch, which is also occasionally used in rubber mixings. This can be ascertained by mixing 5 grms. of the tar with 15 grms. of aniline, or by boiling 5 grms. of the boiled tar or pitch for a few minutes with 25 grms. of aniline, and pouring the solution in a small dish of unglazed porcelain. The solvent, together with the soluble constituents of the tar, is absorbed by the porous dish, while the carbonaceous matter remains behind as a coherent, laminated mass, which, by means of a horn spatula, can be transferred without any loss to a weighed watch-glass, and after several hours' drying in a water oven, weighed until constant.

III. **Extraction with Alcoholic Potash.**—This extract contains what is at present the most important class of organic filling materials for rubber goods, and which comprises the triglycerides of a variety of unsaturated fatty acids transformed into fairly resilient and insoluble compounds, either by the addition of oxygen, of sulphur, or of sulphur monochloride.

Of these three classes of fatty substitutes, the oxidised oils and the chlorosulphides (white substitute) may occur in either warm or cold cured goods; the sulphides (brown substitute) are found in hot cured goods only. Not infrequently mixtures of two of these substitutes are used.

The identification of these substitutes in the extract depends upon the fatty acids obtainable from the saponification products still possessing the

essential chemical characteristics of the original substitutes. We therefore find that:

1. The fatty acids obtained from *oxidised oils* are either entirely free from sulphur or chlorine, or contain only very small quantities of these elements, the presence of which is due to the influence of the sulphur, or of the chloride of sulphur, upon the oxidised oil during the process of vulcanisation. In oxidised oil substitutes the percentages of chlorine or sulphur present, therefore, rarely exceed 0·5 per cent.

2. The fatty acids from the class of substitutes which I described as *sulphide substitutes* (brown substitutes) contain essentially the same quantity of sulphur as the substitutes themselves—*i.e.*, from about 4 to 9 per cent.—but they are entirely free from chlorine, or, at least, practically so.

3. The fatty acids of the *chlorosulphide substitutes* (white substitutes) still contain practically the whole of the sulphur of the original substitute, but the greatest part of the chlorine has been eliminated by the saponification process, and can be determined in the saponification liquors by the usual means.

It will be seen, therefore, that the identification of the oxidised oil substitutes and of the sulphide substitutes offers not the least difficulty if they are present by themselves only. Equally simple is the detection of chlorosulphide substitutes in cold cured articles, but their use in hot cured goods is apt to lead to not inconsiderable analytical complications.

It has been shown (*see* page 146) that the chlorosulphide substitutes at vulcanising temperatures evolve a more or less considerable proportion of their chlorine in the form of hydrochloric acid.[1] Henriques[2] surmised, erroneously however, that the chlorine thus evolved is altogether lost. In fact, scarcely a trace of it disappears, it being almost completely taken up by the india rubber forming a polyprene hydrochloride. If such a sample should contain at the same time substances like zinc white or litharge, a small but distinct proportion is absorbed by these compounds. Anyhow, it will be observed that in cases like these only the sulphur of the substitute is found where we should expect it, the chlorine having migrated to the india rubber to such an extent that its presence is either not recognised at all, or misinterpreted as being due to the vulcanisation of the sample by the cold process. The consequence of this mistake is the misinterpretation of the chloride substitute as a sulphide substitute.

It is therefore evident that for the purpose of distinguishing between a sulphide substitute and a chlorosulphide substitute, some information beyond that obtainable from the components of the extract derived from

[1] Chlorosulphide substitutes prepared from different oils show rather considerable variations respecting the proportion of their total chlorine given off by them at vulcanising temperatures. Thus, colza oil substitutes lose about 80 per cent.; cotton seed substitutes, about 94 per cent.; castor oil substitutes, practically the whole of their chlorine.

[2] *Chem. Zeit.*, 1893, No. 40.

the treatment with alcoholic caustic potash is required. It will be seen that this information is yielded partly by the estimation of the sulphur and chlorine in the india rubber (section VI. of the analytical scheme on page 255), partly also by purely technical considerations.

In this relation it is clear that if there is no chlorine in the india rubber in a quantity about equal to the amount of sulphur in the saponification extract, the substitute indicated by the latter cannot be a chlorosulphide substitute, but must be a sulphide substitute. Of course it might be suggested that a rubber article containing a sulphide substitute might be vulcanised with chloride of sulphur, in which case, according to the above proposition, the substitute would be misinterpreted as a chlorosulphide substitute. I have, however, already stated that sulphide substitutes are unsuitable for, and therefore never used in, mixings to be vulcanised by the cold process. As there is, however, no telling what might or might not be attempted in rubber mixings, attention should be drawn to the fact that cold cured rubber goods yield either no free sulphur at all, or only quite infinitesimal quantities of it, in the acetone extract. On the other hand, both sulphide substitutes and hot vulcanised india rubber goods contain substantial amounts of free sulphur, so that in such a doubtful case the amount of sulphur in the acetone extract would not fail to attract attention.

Of course where there is no chlorine to be found in the india rubber, the identification of the substitute from the indications furnished by the saponification extract is perfectly simple and obvious. In a very large number of cases the interpretation is at once simplified by the fact that the article under examination is of a thickness which would not admit of its vulcanisation by the cold process, which is applicable only to very thin rubber structures, such as waterproof cloth, tobacco pouches, toy baloons, and the like. Articles of greater thickness can only have been produced by the process of hot vulcanisation, and any chlorine they contain must be derived from chlorosulphide substitutes in them.

The presence of a chlorosulphide substitute in a cold cured sample of india rubber is, of course, equally simple to detect. It is characterised by the fact that chlorine and sulphur (not including the sulphur in inorganic compounds) are present in approximately equal amounts, the total of which is, however, considerably in excess of the corresponding total which could be due to the chlorosulphide substitute alone. Nevertheless, it must be stated that this circumstance alone is not invariably sufficient to arrive at a certain conclusion, for the simple reason that the sum of the percentages of chlorine and sulphur in chlorosulphide substitutes may vary, according to the nature of the oil employed, from about 8 to 18 per cent., although the bulk of the chlorosulphide substitutes give figures varying within a narrow margin around an average of about 15 per cent. Conclusive evidence is, however, to be found in the fact that in a sample constituted as above, the ratio of chlorine to sulphur in both saponification

extract and in the residual india rubber is approximately the same as in sulphur monochloride—*i.e.*, sulphur is present in about equal parts.

If a sample contains mixtures of these various fatty substitutes, their identification becomes, of course, somewhat more difficult, and, indeed, in certain limiting cases practically impossible.

The easiest to detect are mixtures of the chlorosulphide substitutes with either the oxidised oil substitutes or the sulphide substitutes. Mixtures of both these descriptions are frequently used in hot cured goods.

The presence of oxidised oil substitutes, together with chlorosulphide substitutes, has, of course, simply the effect of making the ratio between the total fatty substitute present, inclusive of the chlorine in the india rubber, and the sum of the sulphur and chlorine in them, appear proportionately low. We obviously obtain the quantity in which each of these substitutes is present by calculating the amount of chlorosulphide substitute corresponding to the sum of the sulphur and chlorine in the substitute. In doing this, the sum of these constituents in a normal substitute is taken to amount to 15 per cent., and by multiplying the sum of these constituents, as analytically ascertained, by the factor 6·6, we obtain the quantity of normal chlorosulphide present. The difference between this product and the total amount of substitute ascertained is assumed to be oxidised oil substitute.

This might appear a very arbitrary proceeding, seeing that chlorosulphide substitutes themselves may contain very much less than 15 per cent. of chlorine and sulphur collectively. But, in reality, this procedure is not so arbitrary as it looks. It is only the chlorosulphides of the triglycerides, of oxy-acids, or of partially oxidised (blown) oils which contain less than 15 per cent. of sulphur and chlorine combined; and although, from the point of view of ultimate chemical constitution, this calculation would perhaps not be permissible, I have in very numerous practical experiments never been able to discover the slightest difference between the effect in a rubber mixing of a certain weight of (supposed) homogeneous chlorosulphide substitute containing only 9 per cent. of chlorine and sulphur combined, or an equal weight of a mixture of 60 parts of normal substitute (containing 15 per cent. of chlorine and sulphur combined) with 40 parts of oxidised oil substitute. In fact, the above calculation may be taken in the sense of either of these two possibilities from the purely analytical, as well as from the technical, points of view.

The very frequently occurring presence of a mixture of sulphide substitute and chlorosulphide substitute in rubber samples is equally easy to establish. As the sulphide substitute also contains sulphur, it is evident that we must calculate the amount of chlorosulphide substitute present by calculating the amount of chlorosulphide substitute corresponding to the amount of chlorine present, taking in this case, of course, the normal chlorosulphide substitute as containing 7·5 per cent. of chlorine. The

difference between the amount of chlorosulphide substitute thus calculated and the total amount of substitute as estimated represents the amount of sulphide substitute present.

India rubber articles containing mixtures of oxidised oil substitutes and sulphide substitutes are always hot vulcanised. The characteristic feature of the saponification extracts lies, in this case, in the abnormally low percentage of sulphur in the fatty acids. But, in the chapter on india rubber substitutes, I have shown that the amount of sulphur in the sulphide substitutes (brown substitutes) is apt to display as great variations in the percentage of sulphur as do the chlorosulphide substitutes, in respect of the percentage of the sulphur monochloride they contain, and for the same reasons. Sulphide substitutes prepared from the unsaturated oils in their natural condition contain much more sulphur than those prepared from partially oxidised (blown) oils. If we take, therefore, the percentage of sulphur of a normal sulphide substitute as 15 per cent., and calculate upon this basis, and upon the basis of the amount of sulphur ascertained in the saponification extract, the amount of normal sulphide substitute present, the figure thus arrived at, deducted from the total saponification extract, gives us the amount of oxidised oil substitute present. In this case also such an interpretation may be chemically correct, although not so technically. In other words, in the manufacture of the sample, a sulphide substitute prepared from a partially oxidised oil may have been used, and not a mixture of a normal sulphide substitute and an oxidised oil substitute. On the point of fact this ambiguity is quite irrelevant, as the same technical effect is obtained in either case.

Occasionally it may be desirable to characterise somewhat more definitely the nature of a substitute contained in manufactured india rubber. This is, however, only worth attempting in cases where the analysis has shown one only of these substitutes to be present. To identify the oils from which fatty substitutes have been prepared in mixtures of the free acids of the latter, our present methods of oil analysis are, however, quite inadequate.

Where an examination in this direction appears desirable, the most satisfactory method consists in submitting the free fatty acids isolated from the saponification extract to HÜBL'S iodine absorption test. The preliminary operation is carried out as follows:—

The saponification extract is evaporated to dryness, redissolved in water, the solution acidulated with dilute sulphuric acid, and extracted in a separating funnel with ether. The ether solution is dried by adding to it some granulated calcium chloride, and allowing it to stand for a few hours. It is then filtered through a dry filter, the ether evaporated, and the residue, consisting of the fatty acid of the substitute, then dried for a short time in a water oven until all smell of ether has completely disappeared.

A part of this extract is weighed in a flask and subjected to the iodine

absorption test, for the details of which some standard work on oil analysis should be consulted.[1] The figures thus obtained should be compared with the iodine absorption of the fatty acids of substitutes of known composition. A few such determinations are given in the table on page 147.

Incidentally it may be remarked here that before saponifying a fatty substitute for the purposes of the above determination, it is absolutely essential to first submit the substitute to an extraction with acetone so as to remove free fatty oils and sulphur. Unless this is done, the iodine absorption standards are useless for comparison with the corresponding figures obtained with the free fatty acids extracted from manufactured india rubber by means of alcoholic potash.

IV. **Extraction with Nitro-naphthalene.**—The extraction with nitro-naphthalene, or boiling nitrobenzene, results in the solution of the vulcanised india rubber in the solvent named. The process is not attended by the evolution of sensible quantities of hydrogen sulphide or hydrochloric acid. If the sample dissolves without leaving an appreciable amount of mineral residue, the mineral matter present cannot exceed 1 per cent., and this result should be confirmed by determining, on another quantity of the sample, the amount of ash obtained by incineration. As a matter of fact, seeing that this method of separating india rubber and mineral matter still suffers from various difficulties and drawbacks, it is advisable to check the result of this extraction in every case by an incineration test. Indeed, in all cases not calling for a detailed analysis of the mineral matter, the incineration method may be substituted for this extraction method.

Of far more importance than the investigation of the mineral residue would be a method enabling us to differentiate between the various brands of india rubber which may be present in the nitrobenzene solution. At present we possess no such method. In the first part of this book I have shown that the chemical behaviour of the various kinds of india rubber, apart from the results of vulcanising process, yields not the slightest clue to indicate anything like a chemical difference between the hydrocarbons forming the chief constituent of the numerous brands of india rubber.

Nor does this difficulty become less if we consider the question of differentiating between the proportions of new rubber, and recovered, or simply ground up waste rubber (rubber dust) in a given sample. But while the former problem, the identification of the brand or brands of india rubber in a manufactured sample, must at present be confined to attempting to decide as to whether the india rubber is Pará rubber or not, the probability is that the second problem, the detection of recovered rubber in manufactured articles, will before very long become amenable to analytical treatment. What is particularly required for this purpose is a careful study of the relation of the coefficient of vulcanisation to the tensile strength of the various brands of india rubber, likewise the

[1] Lewkowitsch's *Analysis of Oils, Fats, and Waxes*, 2nd ed., 1895.

influence upon the same constant of admixtures of fatty and other substitutes, and of mineral matter. HEINZERLING and PAHL's tables[1] are a first step in this direction, though not sufficiently methodical for the purpose.

Particularly instructive is the determination of the tensile strength (breaking strain) in conjunction with the elongation or stretch of the sample under test at the moment the break occurs.[2] In this respect I have observed that while the addition of recovered rubber does not particularly affect the tensile strength, it reduces the corresponding elongation the more markedly, the higher the proportion of recovered rubber present.

The appearance of the surface of the rupture is also often highly characteristic. The peculiarly smooth, often almost greasy-looking rupture of articles containing fresh rubber only, rapidly disappears and becomes characteristically rough as the admixture of recovered rubber increases. Admixture of 'rubber dust' is always easily recognisable by a microscopical examination of a freshly ruptured surface. A low magnification of about 30 diameters is quite sufficient. This is obtained with an objective of about 8 mm. (⅓ inch) focus.

All the samples of recovered rubber I have examined contain oil of one kind or another, generally mineral oil or petroleum jelly, not uncommonly resin oil, comparatively rarely fatty oils, in quantities of from 8 to 10 per cent. and more. But it is, of course, rarely possible to decide with certainty whether any such oil discovered in the course of analysis is due to the presence of recovered rubber. Considering, moreover, that an admixture of 10 per cent. of recovered rubber would in the analysis yield 1 per cent. of mineral oil only, it is obvious that no definite conclusions can be based upon the presence of the above named oils in a sample.

Already, in the chapter on rubber substitutes, the fact has been mentioned that recovered rubber undergoes vulcanisation just like fresh rubber. In the same place I have pointed out that the description, often to be met with, of recovered rubber as 'devulcanised' rubber is a fraudulent misrepresentation, as the 'recovery' process leaves the sulphur of vulcanisation quite unaffected. It is therefore obvious that in many cases rubber goods manufactured with a large percentage of recovered material exhibit an abnormally high percentage of sulphur of vulcanisation (coefficient of vulcanisation). This is, therefore, a fairly reliable indication of the presence of recovered rubber, provided the result of the tensile strength test does not indicate overvulcanisation. As a very large proportion of the commercial recovered rubber is manufactured from worn goloshes, the india rubber of which always possesses a high coefficient of vulcanisation, the result indicated above will frequently be observed; it fails, however, if the recovered rubber has been produced from rubber articles possessing a low coefficient of vulcanisation.

[1] *See* page 164 *ff.*
[2] The machine described on page 216 furnishes both these data in one test.

Cold vulcanised rubber waste is also submitted to various 'recovery' processes, and the products are again used in the manufacture of cold vulcanised goods. In this case, however, the detection of the admixture offers no difficulty. Cold vulcanised rubber in the recovery process loses practically the whole of its chlorine, and consequently in cold vulcanised rubber goods containing this kind of recovered rubber the normal ratio between sulphur and chlorine no longer exists, the sulphur considerably preponderating. Of course this result would be much the same if ordinary recovered rubber were used in cold cured rubber goods.

V. **Extraction with Boiling Water.**—The extract obtained in this operation scarcely calls for any comment. I am not aware that either farina, or dextrine, which is only very rarely present, are more than mere filling materials in a rubber mixing, with nothing to recommend them for the purpose.

VI. **Mineral Matter.**—This group comprises filling materials, inorganic substances acting as filling materials and at the same time as sulphur carriers, sulphur carriers proper, and colouring matters.

The first of these three groups calls for no special remarks, and such points as refer to the influence of these filling materials upon the behaviour of the manufactured goods under the various conditions of their practical uses will be better discussed in the next chapter.

It may be taken that all the sulphides of the heavy metals—notably those of antimony, lead, and zinc—act as sulphur carriers. So do, to a lesser degree, all lead compounds, owing to their partial conversion into lead sulphide during the process of vulcanisation. Lead oxide (litharge) is, in particular, very largely used for this purpose. Red lead, the presence of which is not uncommon in 'mechanical' goods, acts, of course, similarly, and at the same time has a hardening action upon india rubber, probably in consequence of its oxidising power. Indeed, the rationale of its employment seems to lie in this oxidising action, which, in articles produced from a 'soft' brand of india rubber, produces a firmness which can be obtained by vulcanisation alone, and with the better brands of india rubber only. The presence of red lead in the mineral matter may therefore be generally taken as an indication that the rubber used in the manufacture of the sample is almost to a certainty of somewhat low quality.

Very remarkable, likewise, is the hardening action of barium oxide, calcium oxide, and magnesium oxide upon india rubber. The two first named substances are always employed in the state of hydrates, the latter in the form of the anhydrous oxide. The quantities used are always very small, rarely exceeding 0·5 per cent., although magnesia is sometimes used in somewhat larger proportions.

The cause of the hardening action of these substances is very obscure. Baryta and lime might be assumed to form sulphides, and then act as sulphur carriers, but in mixing either barium or calcium sulphide with the india rubber, no such hardening effect is noticeable after vulcanisation,

and this would not, moreover, explain the analogous action of magnesia, which does not even form a stable sulphide.

In the presence of calcium carbonate it is often rather difficult to detect such small quantities of caustic lime. In this case, either the residue from the nitro-naphthalene treatment, or a fresh part of the finely ground original sample, is boiled for a short time with a 10 per cent. solution of sugar. Any caustic lime present dissolves in this solution, from which it can be precipitated by the addition of a moderate quantity of a solution of ammonium carbonate. The precipitate, however, is never obtained in the cold solution, but forms only after boiling it for a short time.

In coloured samples of rubber goods [1] it is often desirable to ascertain the nature of the colouring matter present. In 'rubber enamelled' goods the colours of the enamel (suspensions of pigments in thin rubber solutions) may be due either to mineral or lake pigments (aniline lakes), as these 'enamel' coatings are either lightly vulcanised by the cold process, or else 'acidised.' [2] The same is true in regard to coloured cold vulcanised articles of every description. In rubber goods which are coloured throughout their mass, and which have been vulcanised by the hot process, the colours can only be mineral pigments, as even the fastest of lake pigments are more or less seriously affected in the hot vulcanising process, although they stand the cold process very well, almost without exception.

(a) *Examination of Colouring Materials in Hot Cured Goods.*

The colour imparted to rubber goods by antimony pentasulphide (golden sulphide) or vermilion, or by a mixture of the two, is well known, and the presence of either, or both, of these bodies can always be specially confirmed by making a test with a fresh part of the sample.

Brown shades are most usually obtained with ferric oxide, which cannot escape detection in the analysis of the mineral residue. It must, however, be borne in mind that these colours, as used, represent always partially hydrated products, and, moreover, very frequently contain considerable quantities of alumina, aluminium silicate, and similar bodies.

Yellow shades are somewhat unusual, and are almost invariably produced with cadmium yellow. This should also be confirmed by special test. Very occasionally zinc yellow, a double salt of zinc chromate and potassium chromate, is used. Its presence is readily detected by fusing a small quantity of the rubber sample with an intimate mixture of 1 part of potassium nitrate and 2 parts of sodium carbonate. The fused mass is dissolved and filtered, when the presence of a chromate in the rubber sample is at once demonstrated by the characteristic yellow colour of the filtrate. Lead chromates cannot be used in hot cured goods, owing to the action of the free sulphur upon lead compounds.

[1] This has, of course, no reference to goods with surfaces decorated with paints or lacquers.

[2] *See* page 55.

Green shades are almost invariably produced with chromic oxide,[1] very rarely with zinc green, a mixture of zinc yellow (*see* above) with Prussian blue. Which of these two is present may be decided by boiling a quantity of the finely ground sample with caustic soda, when, in the presence of zinc green, a strongly yellow solution is obtained. If this test yields a negative result, another part of the sample is fused with the above mentioned fusion mixture, the melt dissolved in water, and filtered. A bright yellow filtrate is proof of the green present being chromic oxide.

Blue shades are produced with ultramarine only, the very fine cobalt blues being far too expensive. Any blue coloration of rubber may easily be recognised as due to ultramarine by the decoloration produced by moistening a piece of the original sample with dilute hydrochloric acid.

(*b*) *Examination of Colouring Materials in Cold Cured Goods.*

Cold cured goods may contain the same colouring agents as are employed in the coloration of hot cured goods, but in the former a number of mineral pigments may be employed which would not stand the hot vulcanising process satisfactorily. This refers particularly to zinc yellow, zinc green (mixtures of zinc yellow with Prussian blue), chrome yellow, and chrome green (mixtures of chrome yellow with Prussian blue), and Prussian blue. The detection of these pigments offers no difficulty whatever, and follows on the lines already mentioned above. The presence of Prussian blue, whether by itself or in admixture with zinc chromate or lead chromate, is discovered by boiling the finely ground sample with dilute caustic soda, filtering, acidulating the filtrate with dilute sulphuric acid, and adding a few drops of a solution of ferric chloride. Formation of the well-known blue precipitate of potassium-ferri-ferrocyanide proves the presence of Prussian blue in the sample.

It should be noted that in cold cured goods antimony pentasulphide, vermilion, and cadmium sulphide are rarely used. The obvious reason is that, as mere pigments, they are much more expensive than cheaper colouring matters which are available for use in cold cured goods in which there is no need for any sulphur carriers.

Of recent years lake pigments prepared from coal tar dyes have been very extensively employed in the manufacture of cold cured rubber goods. These pigments, which contain the dye fixed upon some inorganic basis, such as alumina, barium sulphate, barium carbonate, or china clay, contain varying amounts of the dyes named from 1 to 30 per cent., and both acid and basic dye stuffs are employed in their manufacture. The presence of such lake pigments is readily discoverable by boiling the ground rubber sample in a test tube with 80 per cent. alcohol, and filtering. Any marked

[1] Or, rather, with GUIGNET'S green, a chromic sesquihydrate $2Cr_2O_3, 3H_2O$. SHIPTON, in A. W. HOFFMAN'S *Report of the Juries*, 1863, p. 75, gives its composition as $3Cr_2O_3 . B_2O_3 . 4H_2O$.

coloration of the filtrate indicates the presence of a lake pigment (aniline lake).[1] If the lake is one containing a basic dye, this alcohol extract is generally very strongly tinted, whereas lakes prepared from acid dyes give only a lightly coloured extract, the coloration being, nevertheless, always unmistakable.

If it is desirable to obtain some more definite information on the nature of the pigment present, the above test should be repeated, and two separate quantities of the sample, the one being boiled with a 1 per cent. alcoholic (80 per cent. strong alcohol) solution of ammonia, the other with a 1 per cent. alcoholic solution of acetic acid. In the first of these solutions the acid dyes dissolve copiously from their lakes, whereas basic dyes yield only more or less discoloured solutions. In the second solution the basic dyes in pigment lakes dissolve very freely, the acid dyes very slightly only, if at all.

By evaporating these solutions on a watch-glass on the water bath, the extracted dyes are obtained in a convenient form for further examination, with a view to the further identification of the coal tar dyes present. This is an operation, requiring, however, much experience of coal tar colours and of their chemical behaviour.

The determination of carbon black (lamp black) or graphite (plumbago) in rubber mixings, whether hot or cold vulcanised, is a matter of considerable difficulty. It is even more complicated when there should at the same time happen to be present one of those peculiar brown pigments known as vegetable brown (Van Dyke brown). That this latter pigment should ever occur together with graphite is most unlikely, although there is no telling what extraordinary combinations may here and there be used in rubber mixings; but the above named class of brown pigments are frequently used in combination with lamp black. But if, to crown all, fibrous organic materials should be added to this complication, the possibilities of chemical analysis are altogether at an end, and we have to fall back largely upon optical methods. The conclusions drawn from the latter require, above all, much experience gained more particularly in the microscopic investigation of the mineral residue derived from rubber samples specially produced with the constituents in question.

Even where lamp black is the only carbonaceous pigment present, its detection is often a matter of no small difficulty, as in a large number of rubber goods not more than 1 per cent. of it is used. Of course in these cases the failure to detect it may be due to various causes connected with the separation of the india rubber from the mineral matter. Where larger quantities of carbon black are present, its detection offers no difficulty, provided the degree of vulcanisation of the sample is such as to render it reasonably amenable to the nitrobenzene treatment.

[1] Very commonly the presence of such lake pigments, especially of such prepared with the basic dyes, already shows itself in the very pronounced coloration of the acetone extract.

In the majority of cases it will suffice to detect its presence, and to form by microscopic examination a rough idea of its quantity. As by this time the other mineral constituents are known, the less experienced worker is advised to prepare an intimate mixture of the mineral constituents present in their ascertained proportions, blend this mixture with varying proportions of lamp black, and compare these blends with the mineral residue under examination. Surprisingly accurate results are obtainable by this method, the error in careful working amounting generally to less than 0·5 per cent. This is, of course, largely due to the enormously fine distribution (covering power) of carbon black, and its very low specific gravity.[1]

Attention must here be drawn to the fact that large quantities of carbonaceous matter are sometimes observed in the mineral residue of samples which, in fact, do not contain a trace of carbon black (lamp black). To this peculiar point I drew attention some years ago, and showed that all rubber samples containing red lead, or highly vulcanised samples containing iron oxide in larger quantities, are apt to show this phenomenon, which is due to the circumstance that at the high temperature of the nitrobenzene or nitro-naphthalene treatment, red lead oxidises, or, rather, carbonises, the india rubber. Ferric oxide does not act in this way in samples which are easily resolved in the nitrobenzene treatment, but in highly vulcanised samples requiring a more prolonged treatment the same action takes place, though in a less pronounced degree than in the presence of red lead.

This matter is of such interest—it shows so clearly, on the one hand, the necessity for the extension of our knowledge of the chemical nature and behaviour of india rubber, and, on the other, the care and circumspection required in the analysis of an india rubber article of unknown composition—as to warrant a discussion of one of the first cases in reference to the above named phenomenon.

Two samples of the same make of steam packing, though not of the same batch, had to be analysed. The first sample (*a*) had undergone viscous decomposition, the second sample (*b*) represented the same article in a perfectly sound condition. The analysis of these two samples produced the following figures:—

	a.	*b.*
India rubber,	9·85 per cent.	12·73 per cent.
Organic extract,	8·35 ,,	2·82 ,,
Mineral matter,	63·11 ,,	62·81 ,,
Carbonaceous matter,	16·79 ,,	19·53 ,,
Total sulphur,	1·89 ,,	2·10 ,,

[1] **HENRIQUES' suggestion to determine carbon black in rubber goods by combustion, weighing the CO_2 obtained, is entirely unreliable, and quite worthless in the case of combinations such as those above named.**

On the face of it, this analysis appears extremely dubitable, if not clearly impossible, for, looking at the normal sample (*b*), the compounding of 12·73 parts of rubber with nearly 63 parts of mineral matter and 20 parts of lamp black is a practically impossible operation. Its accomplishment would, at least, require the addition of a substantial proportion of mineral oil or fatty oil, but of such the organic extract did not contain a trace. On the other hand, the organic extract in *b* would correspond to a rubber containing 18 per cent. of resin. Such a percentage only occurs in one or two of the lowest brands of india rubber, and the preliminary physical examination of the sample plainly indicated that a good medium grade rubber had been employed in its manufacture. Such a rubber would not contain above 6, or at most 7, per cent. of resin. This incongruity seemed strongly to point to something abnormal in the analysis of the sample.

The analysis of the decomposed sample (*a*) showed a minimum of india rubber, a considerable maximum of organic extract obviously due to the decomposition of the india rubber, but also a minimum of carbonaceous matter to an amount much too considerable to be accepted as falling within the limits of probable experimental error. There is, moreover, a peculiar parallelism between the amounts of rubber and carbonaceous matter in the two analyses.

All these facts seemed to point to an identical cause of error in both analyses, which only became intelligible on the assumption either that there was no carbon present, or that rubber had disappeared in one place to reappear in another as carbonaceous matter. This latter supposition seemed perfectly feasible in view of the circumstance that nitrobenzene at the temperature of its boiling point (210° C.) would exhibit a not inconsiderable tendency to oxidise so highly oxidisable a body as india rubber. But in this case reduction products of nitrobenzene, azobenzene, oxyazobenzene, possibly even aniline, would have to be traceable in the nitrobenzene solution. These were, however, entirely absent. There then seemed to remain only the assumption of the rubber sample itself, containing an oxidising agent which became active at the high temperature of boiling nitrobenzene. It appeared, therefore, desirable to reduce the boiling point of the nitrobenzene. This could be done by boiling under a partial vacuum, but a simpler way suggested itself in the employment of a mixture of nitrobenzene with about 5 per cent. of chloroform. Such a mixture shows on a reflux condenser a practically constant boiling point of about 173° C.

With such a mixture the samples were re-examined, with the following result:—

	a.	*b.*
Mineral Matter, . . .	63·33 per cent.	63·02 per cent.

Not a trace of carbonaceous matter was now to be found. As it appeared likely that the detailed analysis of the mineral matter obtained in both these treatments respectively would furnish further information, it was carried out on both samples by subjecting them to the pure nitrobenzene

treatment, another part of the same samples to the corresponding treatment with the above mentioned mixture with nitrobenzene and chloroform. The result in all cases was the same as before: the nitrobenzene treatment yielded a mixture of mineral and carbonaceous matter, the nitrobenzene chloroform treatment yielded a residue of mineral matter only. The determination of the mineral constituents in these four residues gave the following results:—

Treatment with Pure Nitrobenzene.		Sample *a.*	Sample *b.*
Carbonaceous Matter, ...		17·22 per cent.	19·93 per cent.
Mineral Matter, ...	$CaCO_3$	20·78 ,,	21·04 ,,
	$PbCO_3$, PbO	40·27 ,,	41·83 ,,
	PbS, $PbSO_4$	2·10 ,,	1·00 ,,
Total Mineral Matter, ...		3·15 per cent.	63·87 per cent.
Treatment with a Mixture of Nitrobenzene and Chloroform.		Sample *a.*	Sample *b.*
Carbonaceous Matter, ...		Trace.	*Nil.*
Mineral Matter, ...	$CaCO_3$	21·02 per cent.	21·11 per cent.
	$PbCO_3$, PbO	32·22 ,,	31·56 ,,
	PbO_2	9·97 ,,	10·05 ,,
	PbS, $PbSO_4$	1·05 ,,	0·88 ,,
Total Mineral Matter, ... :		64·26 per cent.	63·60 per cent.

At a glance it will be observed that there is a considerable percentage of lead peroxide in the mineral matter isolated by means of the nitrobenzene-chloroform treatment. There is no trace of this peroxide to be found in the mineral matter isolated by the nitrobenzene treatment, but we have here a large amount of carbonaceous matter. The causal connection between the carbonaceous matter observed in the first series, and the lead dioxide found in the second series, is obvious, and justifies the conclusion that this carbonaceous matter is a product of the oxidation of the india rubber by the lead dioxide. The two analyses quoted above, therefore, now assume this quite intelligible form:—

	a.	*b.*
India rubber, . . .	26·64 per cent.	32·26 per cent.
Organic extract, . .	8·35 ,,	2·82 ,,
Mineral matter, . .	63·11 ,,	62·81 ,,
Total sulphur, . .	1·89 ,,	2·10 ,,

Of course the lead peroxide found in these samples was not added to the mixings as such, but, as is customary, in the form of red lead.

Quite recently I have observed an effect very similar to the one above described in the analysis of highly vulcanised brake blocks heavily compounded with ferric oxide. The nitrobenzene treatment only resolved the sample very slowly, and the operation had to be greatly prolonged. At first the treatment took its normal course, a bright brick-red solution (suspension) forming. After about an hour's treatment a change of colour was observed—first into brown, which rapidly darkened into a deep black. Finally, the mineral matter, together with a large quantity of carbonaceous matter, was obtained; the colour of the original sample at once precluded the acceptance of this result as in accordance with the composition of the sample.

These cases clearly show that the nitrobenzene treatment requires careful and critical examination, especially if its completion demands prolonged application.

VII. **Sulphur and Chlorine in India Rubber.**—One of the most important points in rubber analysis is the determination of the combined sulphur, or of the combined sulphur and chlorine in the india rubber. The properties of manufactured india rubber, its suitability for various uses, are much more dependent upon a suitable vulcanisation than upon anything else—at any rate, a badly, insufficiently, or too highly vulcanised india rubber article always represents a bad article. Here, however, we touch at once the main difficulty of the vulcanisation problem, from the technical point of view: a degree of vulcanisation quite unsuitable for a certain article may represent the ideal vulcanisation condition of another article. Such a thing as a standard degree of vulcanisation applying to all kinds, or even to one range, of india rubber articles does not exist. Before long we shall probably be in a position to define the minimum degree of vulcanisation which should be aimed at, in order to obtain the most favourable physical constants for each brand of india rubber combined with the highest degree of chemical stability and inertia. But even these data will not reach their full importance for the purpose of the interpretation of analytical results, until we may be able to discriminate analytically between the different brands of india rubber. Not until then shall we be in a position to define analytically the technical value of manufactured india rubber.

DONATH[1] made an utterly premature attempt in this direction. He suggests that the value of an india rubber article depends upon the quantity of india rubber it contains, and its ratio to the sulphur of vulcanisation, or to the vulcanising metallic sulphides present. The larger this ratio, the larger he assumes the value of the article to be. Indeed, he finds it possible to express the value W of every india rubber article by the simple formula,

$$W = \frac{100 - (S + B)}{S}$$

in which S represents the sulphur present in the article, B the mineral and organic admixtures. This would render the work of analytical interpreta-

[1] *Zeitschr. f. d. Chem. Ind.*, i. [1887], pp. 77, 110, 127.

tion delightfully simple, but, unfortunately, this formula is entirely worthless for the purpose for which it was devised. It is perfectly obvious that, according to this formula, the value of an india rubber mixing before and after vulcanisation would be exactly the same, and quite irrespective of the degree of vulcanisation. It is only necessary to state this, to demonstrate the absurdity of the formula.

The commercial value of manufactured india rubber is simply the sum of the values of its constituents increased by the amount of the factory charges—labour, power, capital charges, rates, depreciation, and administration expenses. The technical value of manufactured india rubber may considerably exceed the commercial value according to the utility or serviceability of the articles concerned.

Of all the constituents of manufactured india rubber, none possesses such a paramount influence upon the general excellence of the product as the sulphur of vulcanisation. We may be absolutely compelled, by the exigencies of practical requirements or appearance, to use filling or colouring materials—*i.e.*, to reduce the commercial value of certain articles—but their technical value remains thereby largely unaffected, provided the degree of vulcanisation produced in them is such as to give them the maximum utility or serviceability for which they are in demand.

The percentage of sulphur combined with the india rubber is, however, no measure of its degree of vulcanisation. The following instance of the analysis of the outer cover of a tire will make this clear :—

India rubber,	54·70 per cent.
Organic extract,	1·34 ,,
Sulphur of vulcanisation,	1·99 ,,
Free sulphur,	2·88 ,,
Total mineral matter,	41·08 ,,
	99·99 per cent.
Organic extract in rubber,	2·45 ,,
Total sulphur in rubber,	8·80 ,,
Coefficient of vulcanisation,	3·63 ,,

Here the sulphur of vulcanisation amounting to 1·99 per cent. gives us no direct idea of the degree of vulcanisation of the india rubber. This we only obtain by calculating the percentage ratio between the amount of india rubber (54·70) and sulphur of vulcanisation (1·99) present, and we obtain in this manner the degree or coefficient of vulcanisation (3·63 per cent.). To obtain a comprehensive view of the distribution of the whole of the sulphur in regard to the rubber, I find it of much value to calculate similarly the percentage ratio between rubber and total sulphur (sulphur of vulcanisation + free sulphur) present. By further applying the same treatment to the organic extract, we obtain another very important ratio—organic extract in rubber—which, in the case of the above sample, enables us to draw the conclusion that the india rubber present is pure Pará, as no other rubber would yield such a low percentage of organic extract.

In samples containing no mineral matter, or in samples the mineral matter of which is free from sulphur, the sulphur of vulcanisation can be estimated directly. If the mineral matter contains sulphur, the indirect estimation described on page 254 has to be resorted to.

In the absence of positive vulcanisation standards, the following considerations must guide us in judging the coefficient of vulcanisation :—As has been pointed out in the first section of this book, with increase of the coefficient of vulcanisation come increase tensile strength, elasticity, and distensibility. This, however, is only true up to a certain point, beyond which there is, first, a rather rapid decrease in elasticity and distensibility, followed soon by a decrease of tensile strength. The following diagram referring to four tire covers of absolutely identical composition as regards the quality and proportions of Pará rubber, total sulphur, and mineral matter, but cured under different conditions, renders this evident.

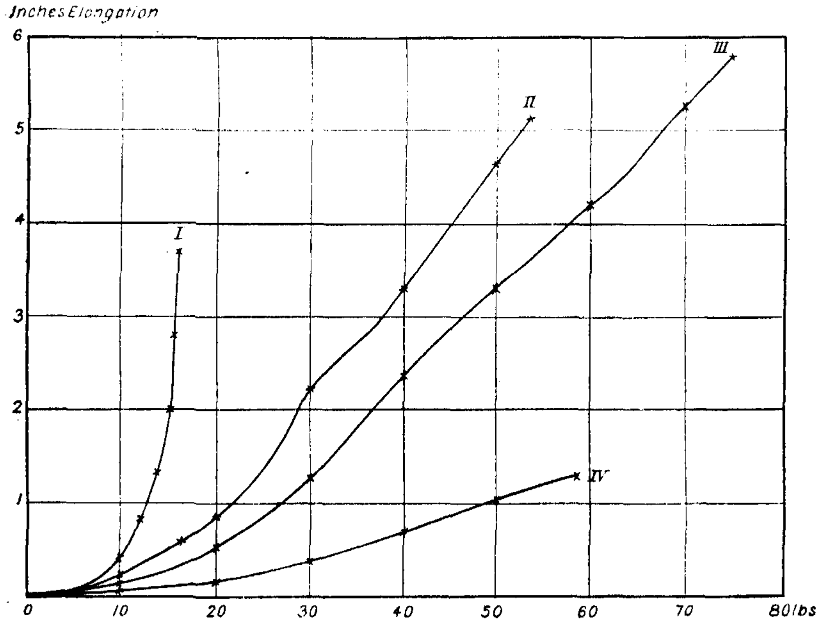

FIG. 26.—Diagram : Tensile strength of differently vulcanised specimens of india rubber.

The vulcanisation coefficients of these four samples are as follows :—

Sample I.,	. . . . .	1·78 per cent.
,, II.,	. . . . .	2·14 ,,
,, III.,	. . . . .	2·87 ,,
,, IV.,	. . . . .	4·44 ,,

Of these, I. and II. are obviously undervulcanised, though II. but slightly; III. is very satisfactorily vulcanised; IV. clearly overvulcanised. It will be seen in every case that the higher the coefficient of vulcanisa-

tion, the higher also the tensile strength for the same distension. This is still true of the overvulcanised sample IV., which, however, already breaks at a distension of 1·25 inches, whereas the two undervulcanised samples, more particularly I., show an inordinate amount of distension under very low stresses. These diagrams may be considered as quite typical for articles known or alleged to be manufactured from Pará rubber, but, of course, other brands of rubber would show different results, although with every brand of rubber the curves of over- or under-vulcanisation would show analogous differences from the curve of correct vulcanisation. Much work remains to be done in this direction.

Overvulcanisation must, however, be clearly distinguished from a high degree, or high coefficient, of vulcanisation, which, of course, is in many articles quite a necessity. Overvulcanisation, in accordance with the results I arrived at regarding the nature of vulcanisation in the first part of this book, does not consist simply in a high coefficient of vulcanisation, but in one obtained under unsuitable conditions, either of temperature, or of time, or of quantity of sulphur. Overvulcanisation may therefore be due to too high a temperature, too long a time, or an unsuitable proportion of sulphur. Of these causes, the one first named is by far the most common, while too short a time is the most usual cause of undervulcanisation.

A high degree of vulcanisation combined with low tensile strength, but fair distensibility, is an almost certain indication that the rubber has been 'overworked' upon the rollers. If, at the same time, the distensibility is low, it is, as far as my experience goes, invariably due to the presence of larger proportions of recovered rubber.

It is evident from the above that undervulcanisation is much more clearly defined than overvulcanisation. This is rather important, as undervulcanised articles are much more prone to 'decomposition' than overvulcanised ones. Indeed, I have never yet seen a case of 'decomposition' due with certainty to overvulcanisation.

Both these faults are much accentuated in goods containing large amounts of mineral matter. The latter always greatly increases the porosity of rubber goods, and therefore also their liability to decay.

Undervulcanised goods containing large proportions of fatty substitutes very rapidly undergo decomposition; overvulcanised goods under the same circumstances suffer very much less.

If there is chlorine in the india rubber, its presence may be due either to the india rubber having been cold vulcanised with chloride of sulphur, or to the mixing containing fatty chlorosulphide substitutes. In the case of articles the thickness of which exceeds a few millimetres, cold vulcanisation is out of the question; but under all circumstances the satisfactory interpretation of the significance of the presence of chlorine in the india rubber is possible on the following considerations.

In articles free from fatty substitutes, the presence of chlorine in the india rubber is a certain proof of the vulcanisation having been effected

by the cold process. 'Rubber enamelled' goods should, however, never be analysed in this connection simultaneously with their enamel coating, but the latter should be carefully pared off. The reason for this is that rubber goods (enemas, etc.), the body of which has been hot vulcanised, often receive a 'rubber enamel' surface coating, generally coloured, which is then cured by the ordinary cold process, or by the 'acidising' process (hypochlorous acid). For this reason an article should not be pronounced as 'cold cured' unless the 'sulphur of vulcanisation' present approximates very closely in amount to the 'chlorine of vulcanisation.'

In articles containing fatty substitutes, the correct interpretation of the analytical results obtained is not so simple. The presence in the rubber of sulphur and chlorine in approximately equimolecular proportions is conclusive evidence of cold vulcanisation only if the alcoholic extract is free from chlorine, or, in other words, if there are no chlorosulphide substitutes present, as it is quite conceivable that in the presence of the latter the amount of hydrochloric acid evolved during hot vulcanisation, and absorbed by the india rubber, might coincidentally be equivalent to the coefficient of vulcanisation of the rubber. This point must not be lost sight of when pronouncing a specimen of rubber as cold vulcanised. The mere fact that it contains chlorine is no proof to that effect, and the overlooking of this point has often led to gross mistakes being made.

Indeed, the only satisfactory criterion which enables us always to decide with certainty upon the question under discussion is that obtained from the amount of free sulphur as ascertained in the 'acetone extract.' In cold vulcanised goods free sulphur is rarely absent, but its quantity is always very small, rarely exceeding 1 per cent. On the other hand, hot vulcanised goods containing chlorosulphide substitutes always contain more or less considerable quantities of free sulphur, for reasons connected with the composition of the mixings required to ensure a thorough vulcanisation. If, therefore, there is any doubt respecting the vulcanisation of a given sample of manufactured rubber, the amount of free sulphur ascertained in the sample readily supplies the required answer.

The following typical analyses will make this clear:—

	Tobacco Pouch.	Garden Hose.
India rubber,	50·22 per cent.	31·29 per cent.
Organic extract,	4·88 ,,	7·34 ,,
Fatty substitute,	37·21 ,,	28·90 ,,
Mineral matter,	2·19 ,,	26·28 ,,
Free sulphur,	0·27 ,,	1·83 ,,
Sulphur of vulcanisation,	2·72 ,,	2·15 ,,
Chlorine in rubber,	2·50 ,,	2·20 ,,
Free sulphur in rubber,	0·53 per cent.	5·84 per cent.
Coefficient of vulcanisation,	5·41 ,,	6·87 ,,
,, chlorination,	4·97 ,,	7·03 ,,

The analytical data[1] above quoted at first sight appear to refer, if not to two similar qualities of rubber goods, at any rate to two similar types, and the inexperienced analyst might well feel tempted to interpret both of them as cold vulcanised articles. Even the coefficients of vulcanisation and chlorination taken conjointly would appear to be well in keeping with this interpretation. But the 'free sulphur in india rubber,' while supporting this assumption entirely in the case of the tobacco pouch, renders it clearly untenable in the case of the garden hose. Such an amount of free sulphur can be present only if sulphur, as such, has been added to the mixing for the purpose of hot vulcanising. The garden hose must therefore be pronounced a hot vulcanised article, and from the presence of chlorine in the india rubber, it follows that the fatty substitute is a chlorosulphide substitute. This conclusion, it may be remarked, in the above case was fully confirmed by the detailed analysis of the 'saponification extract.'

There remains to be mentioned the not very common case of rather small quantities of chlorine, rarely exceeding 1·5 per cent., occurring in samples which either contain no substitutes at all, or no chlorosulphide substitutes, while, at the same time, the combined sulphur in the rubber greatly exceeds the amount of chlorine present. The interpretation of this observation is that the vulcanisation of such a sample is essentially a hot vulcanisation, but that, for reasons connected with the technical conditions of the vulcanising process, the articles have been subjected to a 'surface hardening' produced by 'semi-curing' them—*i.e.*, treating them with a weak solution of sulphur monochloride. The surfaces thus hardened are in this manner protected against mechanical injury.

Of course in hot vulcanised goods containing chlorosulphide substitutes this treatment could not be discovered. This inability is, however, of little moment, as the treatment in question is merely a technical artifice, and has no perceptible influence upon the physical constants of the articles in question.

Unusual Constituents of Rubber Goods.

An exhaustive description of all the substances which are, or have occasionally been, introduced into rubber mixings is almost an impossibility. There is no substance which lends itself so readily to admixture with the most heterogeneous substances imaginable, and this quality leads occasionally to absurdities in this respect which surpass similar abuses in any other technical material known.

In a steam packing which enjoys a not inconsiderable popularity, I found considerable quantities of brass filings and coke powder. A specially 'cheap' bicycle tire contained, besides a very generous allowance of fatty

[1] I have purposely omitted the analytical composition of the fatty substitutes, so as to render more clear the point at issue.

substitute, 10 per cent. of cork dust. Quite a number of supposed high class tires on the market at present contain from 10 to 15 per cent. of paraffin wax. This, it is alleged, will prevent 'suncracking,' but however that may be, it certainly produces a poor tire. A 'metallic' rubber packing contained 35 per cent. of metallic zinc (zinc dust). In various other goods I have detected caseïne, caseïne lime, cork dust, large quantities of tannic acid, glass powder, alum, cholesterine (wool grease), bone ash, mica, and orpiment. The last named substance, arsenic trisulphide, was found to the amount of 6·5 per cent. in a specimen of waterproof cloth for ladies' wear. It is impossible to assume that any manufacturer would knowingly employ such a substance, and I surmise that he was induced to buy it under the guise of some innocently sounding name. Indeed, within my knowledge this substance has been, and is still, offered under the very inoffensive description of 'yellow antimony.'

(*e*) **Defects in India Rubber Goods.**—The most usual defects occurring in manufactured india rubber may be arranged under the following heads:—

a. Defects in the rubber mixings.
b. Defects due to faulty vulcanisation.
c. Defects due to faults of the constructive materials.
d. Defects arising in use.
e. Defects in appearance.

a. Defects in the Rubber Mixings.—A rubber mixing must be considered as defective or faulty if either its composition or its physical condition are such as to preclude its vulcanisation into a physically and chemically sound article. Most commonly this defect arises from the mixing having, as a mechanical operation, been carried out negligently. It is, of course, often extremely difficult to produce a homogeneous mixture of india rubber with pulverulent admixtures. In many cases this could only be done by working the mixture between the rollers for such an inordinate length of time as to produce in the india rubber the often fatal phenomenon of fatigue (*see* page 93) generally described in the trade as 'killing the rubber.' But if we find in different parts of a sample of manufactured rubber a considerable variation in the several mineral, or, more generally speaking, non-rubber, constituents, it is obvious that the mixing in respect of these non-rubber admixtures has been imperfectly carried out. For this defect there is no excuse, and, at the same time, it will be readily understood it is highly detrimental to the production of a sound article. Very often this defect is the cause of premature decay in rubber goods, and the fact that it is so very common tends to show how little its significance and consequences are realised.

The evils arising from a too prolonged working of a rubber mixing, alluded to above as fatigue, although their true nature has up to now been entirely misunderstood, are well known to every experienced rubber worker, and consequently this defect, at least in a pronounced form, is comparatively rarely met with. From what has been said in reference to

this subject on page 94, it will be readily understood that this defect is characterised by well-marked physical signs of undervulcanisation in the presence of a percentage of combined sulphur in the india rubber suggesting a thorough degree of vulcanisation. Manufactured india rubber showing these characteristics is extremely prone to premature decay.

Not very common is the fault arising from the use of slightly damp powders in india rubber mixings. Under the influence of the heat and pressure of the rollers, they form minute hard flakes, which remain embedded in this state in the india rubber. In articles in which a perfect surface is required, these flakes are, of course, highly objectionable, even more so in sheets or strips for rubber insulated cables, in which case they very generally result in 'weak spots,' often in short circuits.

b. Defects due to Faulty Vulcanisation.—As the result of the vulcanisation process is determined by the proportions of sulphur and rubber used, the temperature employed, and the time allowed, but further also by the physical condition of the india rubber, it is evident that with such a number of co-determinants, the number of possible defects must be very large—the more so, as very few brands of india rubber behave similarly, or yield similar results, even when treated under equal vulcanising conditions. It is therefore not surprising to find that probably more than one half of all the defects observed in india rubber goods arise from some defect in its vulcanisation. A very large number of these defects may, moreover, be described as either over- or under-vulcanisation, and be identified, on the one hand, by the vulcanisation coefficient; on the other hand, by the tensile strength and elongation tests (*see* diagrams, fig. 284). To exactly describe the more particular cause of either of the two above named defects is often very difficult, but in many cases a careful study of the coefficient of vulcanisation, the total sulphur in rubber, and of the mechanical tests (tensile strength and elongation) will give valuable indications. In this respect it must be remembered that overvulcanisation in the presence of a large amount of total sulphur is due either to too high a temperature or to too long a time, but in the presence of a moderate or small amount of total sulphur, the fault almost invariably lies in the employment of too long a time. Undervulcanisation in the presence of a large amount of sulphur is due either to too low a temperature or to too short a time; in the presence of a moderate or small amount of total sulphur, either this amount of sulphur itself is too small, or the two before named causes concur. Somewhat similar in its effect to overvulcanisation is the very curious defect arising from vulcanisation at too high a temperature or too long a time, in the presence of too little sulphur. We obtain, then, the peculiar result of a 'rotten' vulcanisation product possessing all the characteristics of overvulcanisation, but differing from it by a low coefficient of vulcanisation. On the other hand, undervulcanisation is often suggested by the physical constants of samples, which, on analysis, are found to be fully vulcanised with a full allowance of

total sulphur. This is very frequently an indication of the phenomenon of 'fatigue,' but by no means always.[1] The physical effect due to the same vulcanisation coefficient is apt to vary considerably in different brands of india rubber, and a percentage of combined sulphur which in Pará would represent a very full degree of vulcanisation, would leave Beni River or Manao rubber rather undervulcanised.

Turning to the defects arising from faults or faulty conditions in the cold process of vulcanisation, we find that the diagnosis of over- or under-vulcanisation is very much simpler in some respects, but complicated by the fact that some brands of india rubber form very unstable vulcanisation products when vulcanised with sulphur monochloride; and further, that sulphur monochloride being a very reactive body, is apt to cause secondary reactions, and act in various ways not intended in its employment.

Cold cured goods—waterproof fabrics, tobacco pouches, gas tubing, and similar articles—are in less need of tensile strength than of softness, pliability, and chemical stability. The behaviour of cold cured goods exposed to the heat of a water oven for from 8 to 10 hours furnished much information on this point. In the case of undervulcanisation, the articles become more or less rapidly very limp, and occasionally almost plastic under the influence of the heat. Moistening them with benzene, and continuing the heating for a few minutes, renders them distinctly sticky. In this test overvulcanisation results in the article becoming either very stiff, sometimes almost brittle, or else very tender and lifeless. The latter is generally observed in the case of goods manufactured from india rubber unsuited for cold vulcanisation.

If effective precautions are not taken to prevent the formation of dew upon the articles during the process of cold vulcanisation, part of the sulphur monochloride is decomposed before it is able to combine with the india rubber.[2] The hydrochloric acid thus liberated is at the root of many of the defects in cold cured goods. If these contain zinc oxide or ferric oxide, any hydrochloric acid produced may lead to the formation of zinc chloride or ferric chloride respectively, both of which are absolutely fatal to cold cured goods.

But even if no formation of dew and consequent decomposition of sulphur monochloride takes place, the interaction of the latter with certain other substances which may form part of the mixing will often produce disastrous results. In this respect copper and manganese compounds and red lead must be mentioned. The first two occur not infrequently as impurities in certain pigments and compounding materials

[1] This phenomenon can easily be studied by exposing a rubber article containing a moderate amount of total sulphur for one or two days to a temperature of about 90° C. in a water oven. The outer covers of bicycle tires, stripped of their fabrics, are very suitable for this experiment.

[2] The formation of this dew is caused by the considerable fall of temperature produced by the rapid evaporation of the carbon bisulphide.

used in rubber mixings; while red lead is often deliberately added, under the assumption, no doubt, that what is, under certain circumstances, a useful constituent in a mixing for hot vulcanisation, must also act beneficially in the cold process of vulcanising.

c. Defects due to Faults of the Constructive Materials.—The only kinds of constructive materials to be considered are the various textile materials used either for the strengthening of rubber structures or for the production of waterproof fabrics.

In undyed textile materials the only defect likely to occur is loss of strength during the vulcanising process. This in hot cured goods is unavoidable, especially if the fabrics are cotton fabrics. The tendering in this case is, of course, due to the action of the vulcanising heat (say 130° C.) for a more or less considerable time upon the cotton, which at temperatures above 80° C. becomes increasingly sensitive to heat. If the loss in tensile strength caused by the vulcanisation process exceeds 15 per cent., the textile material in question may be considered to be at fault. On the other hand, there should be no tendering of the cloth in cold cured goods, and its occurrence is in such articles due simply to some fault in the vulcanisation. Either the chloride of sulphur is of unsuitable quality, or the vulcanisation has been carried out under conditions favouring the deposition of dew upon the rubber coating. The hydrochloric acid thus formed, coming subsequently in contact with the face of the fabric, then attacks the cotton fibre. The defect in this case is therefore entirely the fault of the rubber manufacturer. If, however, the selvage of the rubber-coated fabric is essentially stouter than its body, it often happens that this selvage is not covered by the india rubber coating. On cold curing such cloth, the selvages are liable to take up some of the vulcanising solution, with the result that the cloth along the edges contains chloride of sulphur, the decomposition of which results in the formation of hydrochloric acid, which then destroys the fibre. This effect often spreads for a considerable distance from the edges to the centre of the cloth, so that, on superficial examination, it may sometimes appear as if the cloth were tendered all over. But whenever this tendering is due to an absorption of the vulcanising solution by the selvage, it will be found that the central part of the fabric shows either no tendering at all, or a very slight degree of it only, with a very marked increase of it towards the edges.

In dyed waterproof fabrics (macintosh cloth) tendering is much more frequent. It occurs but rarely in cold cured goods, and then always through one of the two above stated causes—most generally through badly carried out vulcanisation. In hot cured goods it is rather common. It is seldom due to the inferior quality of the yarns used in the manufacture of the textile fabrics, but arises almost invariably from the presence in the cloth of small quantities of sulphuric acid, or from the employment of mordants which at vulcanising temperatures attack the textile fibres. The presence of sulphuric acid in these cases is obviously due to the imperfect

washing of the cloth after dyeing. This is confirmed by the fact that the dyed fabrics showing excessive tendering in the vulcanisation process, due to the presence of free sulphuric acid, are woollens or unions.[1] The amount of sulphuric acid thus present very rarely exceeds 0·25 per cent., an amount which appears to be quite unobjectionable while the fabrics contain their normal proportion of atmospheric moisture. In the process of vulcanisation, however, this moisture, which serves as a diluent for the sulphuric acid, disappears, and the acid rapidly attains a concentration fatal to the textile fibre. This is naturally, therefore, most pronounced in the case of unions, and results in extreme cases in the almost complete destruction (carbonisation) of the cotton warps.

Among mordants having such a tendering effect, ferric oxide is to be particularly mentioned. At vulcanising temperature this substance affects cotton fibre materials very energetically. Wool seems to suffer much less. Whether the enormous tendering of heavily loaded black silk is to be ascribed to the tin and iron mordants used, I have not sufficient experimental data to decide, but the probabilities are in favour of the assumption.

d. Defects arising in Use.—The discussion of all the defects coming under this head would, in itself, fill a fair-sized volume. No doubt the composition of india rubber articles of every description is, at times, such as to render them more or less unsuited for their purpose, or, at least, to favour the development of certain defects; but I am not sure whether cases, in which the appearance of defects is not so much the fault of the rubber manufacturer as of the consumer, are not much more numerous. There is, to begin with, the fatal tendency on the part of the consumer to buy increasingly cheaper grades without the slightest consideration of the market prices of crude india rubber, and there is, moreover, the unconscionable treatment to which rubber goods are often subjected. Indeed, it is very doubtful whether there is any other class of goods which is so habitually maltreated as rubber goods, from which a great number of people appear to expect the properties of almost all the other technical raw materials combined.

Defects arising from use alone may be due to sins of omission or commission in respect of the constituents of the mixings, or to unsuitable vulcanisation. That is to say, considered from general points of view, a sample of manufactured rubber may in every respect appear a thoroughly satisfactory production, and nevertheless prove unsuited to the special requirements and conditions of its practical use. In such cases the defect obviously arises from the circumstance that in its composition and manufacturing treatment insufficient attention was paid to the chemical and physical influences to which it would be exposed in practical use, or else

[1] In the dyeing of cotton fabrics, sulphuric acid is only very rarely used. If used, it is easily removed by washing, whereas it clings pertinaciously to wool. This, no doubt, is due to functional chemical differences between vegetable and animal fibres.

the consumer himself uses an article manufactured to meet other and different requirements.

The defects in question may be caused by the following chemical agencies:—

1. **Acids.**—The action of the various acids upon manufactured india rubber varies considerably according to the nature of the acid, and, for the same acid, with its concentration, and with the temperature at which it is applied. The latter point is rather important, as will be seen on examining the first of HEINZERLING and PAHL's tables given on page 165. From the figures there given for the action of sulphuric and acetic acid respectively, one might feel justified in drawing the conclusion that the action of sulphuric acid upon manufactured india rubber invariably produced a decrease in weight, the action of acetic acid almost as invariably an increase in weight, in the test piece. But this conclusion would be entirely erroneous. The above named authors, to begin with, operated with concentrations of these acids (27·5 per cent. H_2SO_4, and 46·5 per cent. $C_2H_4O_2$) which cannot be said to be fairly representative of the conditions most frequently encountered in practice. They altogether omitted the investigation of the simultaneous effect of acids and temperatures up to the boiling point of water. In my opinion, this work should be repeated with acids not exceeding 10 per cent. in strength at the temperatures of say 20, 60, and 90° C. The results of such a series would bear much more clearly and surely upon the behaviour of manufactured india rubber under practical conditions. My own observations leave no doubt that the action of a 10 per cent. sulphuric acid upon india rubber, both at ordinary and at higher temperatures, is much more marked in the vast majority of cases than the prolonged action of 27 per cent. acid in the cold. Treatment of rubber samples, similar in composition to those experimented upon by the above named authors, with a 10 per cent. strong acetic acid has very little effect in the cold, but acts most energetically at temperatures above 50° C., the effect, however, being not an increase in the weight of the sample,[1] but a more or less considerable decrease.

Articles manufactured from sound india rubber and sulphur alone withstand the action of 10 per cent. sulphuric acid even at boiling temperature for very long periods, provided they are reasonably treated as regards mechanical wear. But goods of this high quality are not the rule, the majority of consumers preferring those of a low first cost, and these can only be supplied by resorting to 'mixings' containing more or less considerable quantities of mineral matter, and it is in this class of goods that various defects make their appearance on exposing them under practical conditions to the action of acids.

It is therefore these mineral matters which are primarily responsible for the appearance of defects in rubber articles exposed to the action of dilute acids, such as sulphuric, hydrochloric, or acetic acid; and it is obvious

[1] *See* the extraordinary figures obtained by HEINZERLING and PAHL.

that if the mixings contain any substances easily acted upon by these acids, a more or less rapid disintegration is the unavoidable result. It might be thought, however, that these acids could at most affect merely the surface of the rubber articles, as this substance is generally considered the waterproof substance *par excellence.* This is another of those deep-rooted errors which it is almost impossible to destroy. There are, indeed, scores of substances which, as mere waterproofing agents, are infinitely superior to india rubber, and which absorb scarcely appreciable quantities of water on *prolonged immersion, whereas india rubber under the same conditions may* absorb as much as 25 per cent. of its weight. This absorption is greatly facilitated by an increasing porosity of the india rubber, and as the porosity of india rubber unavoidably increases with the proportion of mineral matter which is worked into it, the action of the acids is by no means confined to the surface only of the articles. If, then, this mineral matter is readily acted upon by acids, the primary nature of their action upon rubber articles is perfectly obvious. This action in its simplest form is simply a dissolving action, but in many cases the products formed by it may exert a secondary action upon the india rubber often more destructive than the first.

Zinc white, Paris white ($CaCO_3$), and lithopone are the greatest offenders in this respect, and they are also used more frequently in rubber mixings, and in greater quantities, than any other mineral substance.

Dilute sulphuric acid will dissolve out the zinc white and the zinc sulphide of the lithopone in the form of zinc sulphate, thus converting the rubber into a finely porous mass, and I look upon this porosity (sponginess) as the immediate cause of the mischief. It not only greatly reduces the resistance of the remaining india rubber to friction and mechanical wear and tear generally, but it lays it open to the influence of oxidation in a peculiarly effective manner. Whether it is merely the enormous increase *of surface which renders india rubber in this state such a certain prey to* oxidation, I am not prepared to insist, but it is an everyday observation that india rubber rendered porous in this manner undergoes oxidation at an extraordinarily rapid rate.[1]

[1] The rate at which a sample of manufactured india rubber, when deprived of the free sulphur which is distributed throughout its mass, will undergo oxidation is perfectly astounding. This observation, that manufactured india rubber, after extraction with acetone or carbon bisulphide, is extremely oxidisable, led HENRIQUES to assume that free sulphur was not only not objectionable in manufactured india rubber, but acted, indeed, as a preservative of it. This assumption I consider entirely erroneous, and I hold that this phenomenon is simply due to the finely porous condition of the india rubber caused by the removal of the free sulphur. This view is confirmed by the circumstance that porosity produced by the removal of any other body present in a state of fine distribution has exactly the same effect. It is also confirmed by the fact that goods, which have been vulcanised in such a way as to contain only just appreciable traces of free sulphur, show for that reason no particular inclination to oxidation ; and it is further supported by the observation, much utilised in practical working, that the admixture to india rubber of substances counteracting incipient porosity by filling up the

The action of dilute sulphuric acid (10 per cent.) upon india rubber containing Paris white leads to the gradual transformation of this substance into calcium sulphate $CaSO_4,2H_2O$. This reaction involves a considerable increase on the bulk of the original calcium carbonate present, and it produces, therefore, a correspondingly considerable internal strain in the india rubber, which renders it apparently hard and inelastic, and reduces considerably its resistance to wear and tear.

Dilute hydrochloric acid (5 to 10 per cent.) dissolves the zinc white as well as the Paris white and the zinc sulphide of the lithopone, and its action is distinctly more rapid than that of sulphuric acid. It is the zinc oxide and zinc sulphide which, in the case of this acid, are most objectionable on account of the formation of zinc chloride, which has a curiously destructive action upon india rubber.[1] Concentrated hydrochloric acid (from 12 per cent. upwards) induces a more or less rapid destruction of the india rubber by converting it into polyprene hydrochloride.

Dilute acetic acid dissolves the zinc white and Paris white, but is without effect upon lithopone. The latter may therefore safely be used in the manufacture of rubber goods required to withstand the action of this acid. Concentrated acetic acid dissolves the zinc white and Paris white rather more slowly than the dilute acid, but it shows the curious effect of inducing a considerable swelling of the india rubber, especially if the latter happens to possess a low coefficient of vulcanisation. This is curious in view of the fact that acetic acid has neither a solvent action nor even a perceptible swelling action upon unvulcanised india rubber.

The above named acids are those to the action of which manufactured india rubber in its technical use is most frequently exposed, and it will have been noticed that any such detrimental action of these acids is due not so much to their direct action upon the india rubber, as to their action on one or other of the mineral matters with which it has been compounded. There are, however, some acids, the action of which is characterised by the circumstance that it affects the india rubber itself rather than the mineral matter present. The acids of this description most likely to be encountered by india rubber articles are chromic acid (including bichromates) and nitric acid. Both rapidly destroy soft rubber goods of every description, nor are any means known of reducing such action to a satisfactory

pores as soon as formed invariably reduces its liability to oxidation. I look upon the admixture of tar, mineral oils, paraffin wax, and similar bodies as substances performing this valuable service.

In this connection it is also worth pointing out that finely ground (vulcanised) rubber waste, which has been boiled with some alkaline solution so as to deprive it of its free sulphur, and which is subsequently dried in a vacuum stove, on being removed from the latter, suffers oxidation at such a rate that, after a few minutes' exposure to the atmosphere, the whole mass reaches a temperature often exceeding 250° C. If this reaction is not checked in time, the rubber bursts into flames.

[1] I am inclined to believe that this action consists in an intramolecular rearrangement of the polyprene complex, more particularly in the commutation of the olefinic polyprene into a cyclical polyterpene.

minimum, still less to prevent it. Hard rubber goods are extremely slightly affected by these acids, evidently owing to the fact that vulcanite constitutes a saturated compound.

It is only to be expected that solutions of oxidising agents in general affect india rubber in much the same way as the two above named acids. This action is very marked in the case of solutions of bleaching powder, ferric salts, nickel salts, cupric salts, and vanadium salts.

2. **Alkalies.**—Dilute solutions of the alkalies have very little action upon manufactured india rubber in the cold. At higher temperatures and concentrations they have a tendency to considerably soften india rubber possessing a low coefficient of vulcanisation, and still more so india rubber containing much free sulphur. India rubber thus softened tends to decay very rapidly.

If the india rubber contains mineral matters which are chemically affected by alkalies, such as zinc oxide and, to a lesser degree, litharge, the articles very generally suffer disintegration, which rapidly proceeds from the surface inwards.

As all the fatty substitutes are saponifiable by alkalies, ammonia excepted, it is obvious that rubber goods coming into contact, especially with hot alkalies, should not contain that admixture. For the same reason such goods should contain no saponifiable resins. In this respect it should be remembered that some brands of india rubber contain saponifiable resins as a natural impurity.

3. **Organic Compounds.**—Generally speaking, all organic substances which are readily absorbed by india rubber tend to deteriorate it, especially at higher temperatures. Fatty, mineral, and resin oils are especially conspicuous in this respect. That these exert any chemical action upon the india rubber is very improbable, but they all soften it, and thereby render it more liable to oxidation. Aniline and similar organic bases act in the same manner, but the surprisingly destructive action upon india rubber of some of them—notably hydrazine and its organic homologues—strongly suggests a direct reaction between them and the rubber substance. The action of all these bodies decreases with an increase of the coefficient of vulcanisation, and the latter, therefore, should be carefully considered in manufacturing goods known to be subsequently exposed to the influence of the above named classes of compounds.

4. **Influence of High Temperatures.**—India rubber articles exposed to high temperatures may develop quite a number of defects. The most characteristic of these are as follows:—

(*a*) The articles, while apparently remaining unaltered, are found, on closer examination, to have lost more or less completely their strength or cohesion.

(*b*) The articles assume a much darker colour, often look as if their surface had been singed, and the latter is more or less sticky.

(c) The articles become hard, frequently cracking on sharply bending or doubling them.

(A) Articles possessing a comparatively low coefficient of vulcanisation are particularly liable to develop this defect, especially if the time allowed for vulcanisation has been short. Much the same phenomenon occurs also in articles containing a considerable amount of paraffin wax (5 per cent. and upwards), or similar hydrocarbons.

(B) This defect is generally associated with goods containing mineral oils, large quantities of recovered rubber, or large proportions of 'sulphide' substitutes.

(C) This last defect invariably appears in goods containing 'white' substitutes (chlorosulphides), but more commonly it is due to the presence of a considerable amount of free sulphur.

The first two defects are fatal to articles which are to be habitually exposed to high temperatures, particularly to high pressure steam. The 'blowing out' of joints is generally the result of the use of this class of goods. Goods showing the second defect require, moreover, a frequent tightening up of the joints, which in this case often results in the packing being pressed some distance into the free lumen of the pipes, thus throttling the flow of steam.

If the defect described above under C is not accompanied by loss of strength, it is not in itself objectionable in steam packing. Indeed, in modern practice the production of goods, which in use form a hard vulcanised joint, is aimed at. These remain absolutely steam proof as long as they remain undisturbed. A typical American product of this description gave, on analysis, the following results:—

India rubber,	8·28 per cent.	Paris white,	19·68 per cent.
Balata,	10·13 ,,	Plumbago,	20·62 ,,
Organic extract,	1·85 ,, [1]	Brass filings,	9·15 ,,
Free sulphur,	2·24 ,,	Total sulphur in rubber,	19·87 ,, [2]
Sulphur of vulcanisation,	1·42 ,,	Coefficient of vulcanisation,	7·71 ,, [2]
French chalk,	26·62 ,,		

The low percentage of resilient substances (rubber and Balata) contained in this packing renders it rather rigid to begin with. This rigidity is subsequently very much increased by the high coefficient of vulcanisation, and in use this steam packing will become harder still as the result of the after-vulcanisation produced by the large amount of free sulphur present.

There are, of course, other classes of rubber goods, the hardening of which under the influence of heat would be highly objectionable, as steam hose, motor car tires.

5. **The Oxidation of Rubber Goods.**—Under this heading are classed a

[1] This evidently consisted of some soft resin such as colophony.

[2] Calculated upon the sum of the percentages of india rubber and Balata.

number of defects which all possess the common characteristic of the rubber, becoming stiff and hard, or else being converted into a more or less sticky and plastic substance.

Whether all, or, indeed, any, of these defects are to be attributed in their final stages to oxidation or not, is uncertain, but they undoubtedly arise in the first instance from a great variety of causes.

That india rubber is extremely prone to oxidation is a matter of every-day observation. Indeed, this is only what the peculiar chemical nature of india rubber would lead one to expect. The more or less pronounced tendency of all terpenes to 'resinify'—*i.e.*, to form resinous bodies by absorption of oxygen—goes a long way to explain the analogous tendency of india rubber. The spontaneous oxidation of the terpenes has been very little studied, but it appears to proceed on lines similar to a great number of other cases in which the formation of hydroxyl plays an important part. The same is, no doubt, true of many of the cases of oxidation in india rubber. Perhaps this explains the very curious phenomenon that india rubber in intimate contact with oxidising bodies invariably becomes oxidised itself. Herein lies one of the most potent reasons against the use of unstable or oxidisable substances in india rubber mixings.

The formation of resinous bodies from india rubber (unvulcanised) under the influence of atmospheric oxygen was first observed by SPILLER (*see* page 9). Subsequently BURGHARDT[1] paid some attention to the technical side of this subject, and he arrived at the conclusion that "the amount of oxygen taken up or combined with the caoutchouc is an index of the amount of deterioration which it has undergone." In support of this statement, he quotes the following analyses :—

	No. 1.	No. 2.	No. 3.	No. 4.	No. 5.
Carbon, ...	87·27	87·50	77·91	72·53	64·00
Hydrogen, ...	12·73	10·00	10·33	11·31	9·26
Sulphur, ...	*Nil.*	2·50	5·15	1·97	2·28
Oxygen, ...	*Nil.*	*Nil.*	6·61	14·19	24·46

No. 1. Pure caoutchouc from Pará.
No. 2. Theoretical vulcanised elastic thread.
No. 3. Vulcanised elastic thread, perfectly sound.
No. 4. ,, ,, damaged, but still elastic.
No. 5. ,, ,, ,, brittle and very hard.

This subject was further investigated by THOMSON,[2] who also observed the marked oxidation by the oxygen of the air especially at higher temperatures. The detrimental effect he ascribes to the air occluded in the pores of rubber goods is, however, greatly exaggerated, as the amount of oxygen thus present, even if it is all taken up by the india rubber, is

[1] *Thorpe's Dict. of Appl. Chem.*, vol. ii. p. 320.
[2] *Journ. Soc. Chem. Ind.*, 1885, p. 710.

far too small to sensibly affect the latter. His suggestion, therefore, to vulcanise rubber goods in vacuo is entirely unnecessary, and it is, moreover, a practical certainty that it would result in the production of an enormous proportion of faulty (blown) goods. THOMSON was also the first to observe that the extraction of the free sulphur renders the rubber liable to very rapid deterioration, and his explanation that this is due to the porosity caused by the removal of the sulphur particles is undoubtedly correct. This is equally true in regard to his statement that the presence of oils, especially fatty oils, in india rubber much increases its tendency to oxidation; and his statement that in this respect palm oil shows the most, and colza oil the least, activity is fairly in accordance with our practical experience—at any rate, so far as the last named of these oils is concerned.

We owe to HÜFNER[1] a quantitative observation of the absorption of oxygen by india rubber. He ascertained that an india rubber stopper of 40·8 grms. weight showed during six months a daily oxygen absorption of 0·074 c.c., or a total of about 14 c.c. = 20 mgrms. This result bears obviously no appreciable relation to the weight of the rubber stopper experimented upon, but only to its surface, which is not stated.

The disastrous effect of copper upon india rubber was first pointed out by BURGHARDT, but it must be remarked that different copper compounds act very differently in this respect, insoluble compounds scarcely acting at all. This is the reason why 'dry heat cured' waterproof fabrics, the cloth of which contains copper, very rarely give trouble on that score, the cupric sulphide formed in the vulcanisation process being practically innocuous. Under the same conditions cupric chloride, which acts as a most energetic oxygen carrier, and rapidly destroys the proofing, would form in 'cold cured' cloth.

In the series of observations on the following page are given the results of a number of tests in this direction made by impregnating scoured, bleached, and carefully washed cotton cloth with solutions of various strengths of cupric sulphate. The fents were then dried, passed through a dilute solution of sodium carbonate, washed and again dried. In the various fents so prepared, the percentage of copper present was estimated. Fents 1 to 9 were spread with pure Pará rubber, and 'cold cured'; fents 10 to 17 were spread with a mixture of pure Pará with 6 per cent. of sulphur, and 'dry heat cured.' These samples were then put by and examined upon from time to time.

The remarkable influence of the mode of vulcanisation upon the activity of the copper will readily be noted; so will the curious fact that so very minute quantities of copper are capable apparently to destroy unlimited quantities of india rubber. Respecting this point, I suspect that the cupric salts in the textile fabrics enter into organic combination probably with acid products of the oxidation of india rubber, and these compounds gradually penetrate into the india rubber, carrying their effect

[1] *Ann. Phys. Chem.*, N.F. xxxiv. 1.

through its whole mass. The action of the cupric salts is, of course, that of the oxygen carrier, and may be expressed by the equations:

$$2CuO = Cu_2O + O,$$
$$Cu_2O + O = 2CuO,$$

which explain why mere traces of copper suffice to destroy an almost unlimited quantity of india rubber. This action of copper in the cloth is enormously accelerated by the presence of oils or greases in the cloth, which no doubt act as an excellent vehicle for the carrying of the cupric salts in the india rubber.

No. of Test.	Per cent. Cu.	Appearance after
1	0·004	6 months : perfectly sound.
		12 ,, : ,,
		18 ,, : ,,
		21 ,, : very slight signs of decomposition.
2	0·008	6 ,, : sound
		9 ,, : doubtful.
		12 ,, : distinctly decomposing.
3	0 010	6 ,, : very doubtful.
		9 ,, : decomposing.
4	0·025	6 ,, : very doubtful.
		9 ,, : badly decomposed, hard.
5	0·03	6 ,, : decomposition very marked.
		9 ,, : quite hard and brittle.
6	0·045	3 ,, : distinctly decomposing.
		6 ,, : badly decomposed
7	0·065	1 month : decomposing.
		3 months : quite hard.
8	0·100	1 month : badly decomposed.
9	*Nil.*	Sound after 6 years.
10	0·004	,, ,,
11	0·008	6 years : distinctly stiffened, but still saleable.
12	0·010	Getting stiff after 3 years ; after 6 years decomposed.
13	0·025	21 months : signs of change.
14	0·030	,, ,, ,,
15	0·045	15 months : distinctly decomposing.
16	0·065	9 ,, : already hard.
17	0·100	4 ,, : distinctly decomposing.

The salts of nickel, manganese, and tin act similarly to those of copper, though in a much less degree. Whether the salts of iron are capable of such action is still doubtful; theoretically one would expect it. Chromic salts are without any action.

Rubber goods containing excessive quantities of heavy coal tar hydrocarbons, mineral oils, fatty oils, or greases, are very liable to rapid destruction by oxidation. Goods of this description will generally be found to be of very low quality, and as the above named oily bodies tend to swell the india rubber, they thereby impart to it a certain softness and resiliency suggesting a better quality. In this swelled state india rubber is particularly sensitive to oxidation.

Fatty substitutes, if present in large quantities, are liable to affect

india rubber in the same way if they contain high percentages of free oils, or if they are chemically unstable.

In a very large number of cases we find, however, india rubber goods suffering rapid destruction from oxidation without there being any of the above named contributive causes present. I believe that in all these cases a faulty vulcanisation is at the bottom of the mischief. Unfortunately neither a faulty, nor, as a matter of fact, a correct, vulcanisation can be defined in simple terms, such as, for instance, may be used respecting the coefficient of vulcanisation. The latter certainly may be evidence of faulty vulcanisation when it is obviously unusually low or unreasonably high, but it is quite conceivable that a piece of rubber may be badly vulcanised though it possesses a satisfactory coefficient of vulcanisation. The physical conditions under which vulcanisation has been carried out exert enormous influence upon the stability of the product, more particularly upon its liability to oxidation, and at the present time we are not yet in a position to ascertain in numerical terms the effect of any possible combination of vulcanising conditions in relation to any given coefficient of vulcanisation.

e. Defects in Appearance.—Defects of this description may be due to mechanical causes, to unsuitable physical conditions (apart from those which may possibly exist in the vulcanising process) during manufacture, or to certain faults in the mixings or curing. We need only concern ourselves here with defects due to the last two causes—indeed, it will be found that as far as blemishes in the appearance of india rubber goods are concerned, the cause lies almost invariably in the vulcanising, and consists generally of some kind of discoloration. These defects appear, therefore, most frequently in white, drab, and coloured rubber goods, and they are caused either by the action of sulphur vapour or by the action of chloride of sulphur, and not uncommonly by the combined action of chloride of sulphur and moisture, upon the pigments and other colouring matters contained in the india rubber. Either these are not able to withstand the influence of these substances, in which case the colouring materials used have been injudiciously selected, or they contain some impurity which is responsible for their discoloration, or perhaps the 'cure' has been too prolonged or carried out at too high a temperature, or the 'cold curing' solution has been too strong or carried out under conditions favouring the deposition of moisture upon the surface of the goods. A careful examination of the goods and of the materials used in the manufacture will in most cases readily furnish the clue to the explanation of the defect.

The appearance of the free sulphur contained in manufactured india rubber upon its surface ('sulphuring up') is in the case of a large number of rubber articles looked upon as an effective finish, in every way to be preferred to the rather crude appearance of the goods fresh from the vulcanising room, as it imparts to them a soft, velvety surface. In many other articles, notably coloured and black goods, this 'sulphuring up' is, however, regarded as a serious defect.

This phenomenon is, of course, due to the excess of sulphur in the vulcanised goods, which, after vulcanisation, gradually changes from the colloidal to the crystalloidal form (*see* page 111), and it is evident that it is closely connected with this change of physical condition, because an unvulcanised mixture of india rubber with crystalloidal sulphur—flowers of sulphur, ground rock sulphur—never sulphurs up. A vulcanised rubber article which has a tendency to 'sulphur up' will not do so for months if it be kept at a fairly uniform temperature in a perfectly dust-free atmosphere, but the moment it is touched by the hand or by a brush, or as soon as it is exposed to dust, the process of 'sulphuring up' begins, and in a few hours will spread all over the surface. At first a very fine film is formed, composed of microscopically fine sulphur crystals, which in course of time (and provided there be a sufficient amount of free sulphur in the article) grow in size until eventually they become plainly visible to the naked eye.

The current notion is that this occasionally very troublesome defect is simply due to the fact that sulphur is slightly volatile at ordinary temperatures. This view I consider entirely erroneous. Indeed, if the extremely slight volatility of ordinary sulphur were the cause of the 'sulphuring up,' we should expect this defect to disappear even at a quicker rate than at which it appears, or, in other words, it could not exist at all. From what has been shown respecting the curious phenomena accompanying the crystallisation of colloidal sulphur (page 110 *ff.*), it is evident that this process of 'sulphuring up' would much more aptly be described as a process of 'sulphuring down'—*i.e.*, the process does not, as is generally suggested, begin below the surface, gradually working its way outward, but it begins at the very surface itself.

The sulphur remaining free after vulcanisation is fairly evenly distributed throughout the india rubber in the form of extremely small globules of colloidal sulphur, and these retain their colloidal state until one or more of them lying exposed on the surface begin to crystallise under the influence of extraneous agencies. Crystallisation once having started on the surface, rapidly spreads over it—at any rate, under the conditions of repeated handlings to which rubber goods are subject in the factory. The action of all these crystallised globules is now exactly identical to those described on page 111 and figured on Plate III.—*i.e.*, the vapour tension of crystallised sulphur being considerably lower than that of colloidal sulphur, every one of them represents the centre of a minimum of vapour pressure, to which, consequently, all the colloidal sulphur from the inside of the rubber article gradually distills, crystallising around it in the well-known dendritical forms. It is therefore evident that the 'sulphuring up' starts entirely from the surface, the colloidal sulphur inside the rubber then, so to speak, condensing on this outer crystalline surface.

Once formed, the permanent removal of this sulphur condensation is an

extremely difficult matter. The remedy therefore lies in the prevention of its formation. This must obviously be possible in one of the following ways :—

(*a*) Vulcanising with as small an excess of sulphur as possible.

(*b*) Vulcanising under such conditions that at the end of the operation all the free sulphur has disappeared.

(*c*) Using rubber mixings containing substances which will chemically combine with the free sulphur.

(*d*) Coating the vulcanised articles with some finish or polish impermeable to sulphur vapours.

(*e*) Employing, in the mixing, substances possessing the property of rendering, after vulcanisation, the free colloidal sulphur crystalline throughout the mass of the articles.

In practice method (*a*) is the one most generally followed, but to be efficacious it requires an extremely nice adjustment of the proportions of india rubber, sulphur carriers, rubber substitutes, and sulphur employed, and of the time and temperature to be allowed for vulcanisation.

Method (*b*) can only be used with goods vulcanised by the 'open cure,' in which the sulphur vapours may freely pass off the vulcanising goods. On a very large scale this method is adopted for the curing of rubber shoes and goloshes.

Method (*c*) would be perhaps the most satisfactory method to employ all round. There are many preparations in the market for the purpose, but, as yet, none of them can be relied upon.

Whether method (*d*) is satisfactory or not depends much upon the amount of free sulphur present, as, at the present moment, we do not know of any absolutely sulphur-proof coating for the purpose.

I am not aware that this method (*d*) has so far designedly been resorted to, but the action it involves does by no means appear impossible of realisation. Its achievement would represent a most valuable technical acquisition.

The defect known as '*rolling*,' or '*cockling*,' which not uncommonly occurs in waterproof fabrics, must also be mentioned here. It is most usually due to shrinkage of the cloth on exposure to rain, in which shrinkage, of course, the rubber coating does not take part. It must, however, be borne in mind that a very similar phenomenon may be produced in the cold curing of proofed cloth, the rubber coating of which has not been dried effectually, and consequently still retains some naphtha. Whether the cause of the rolling lies in the cloth itself or in the proofing, may readily be decided by observing in which direction the cloth rolls. Rolling towards the cloth side is certainly due to shrinkage of the cloth, rolling towards the rubber side to the cold curing of an imperfectly dried proofing.

APPENDIX.

SANITARY CONDITIONS IN INDIA RUBBER WORKS.

In the mind of the general public, an india rubber works is always associated with all sorts of evil smells, and it must, unfortunately, be admitted that there is substantial ground for this indictment, although within the last ten years much has been attempted, and not without success, in mitigation of this state of things. Still much remains to be done. Fortunately, in this respect most manufacturers to-day clearly realise that the existence of insanitary conditions in their workshops is not only reprehensible on ethical grounds, but also a very potent cause of 'slackness,' or loss of power of production, in the work people, though there is still a good deal of indifference with regard to insanitary conditions, the remedy for which is suspected of having 'no money in it.'

In the following pages I propose to deal with the insanitary conditions in india rubber works in the order in which they are likely to arise in the progress of manufacture.

1. **Rubber Washing.**—The first operation the crude rubber undergoes on entering the factory consists in a washing process. As a preliminary, the rubber, if necessary, after being reduced by cutting to pieces of a suitable size, is placed in tanks, where it is boiled with water for a certain time. From these tanks it passes to the well-known washing mills, the washed sheets emerging from which are subsequently dried either in hot-air stoves or in vacuum pans.

The nuisance likely to arise in this process is in the boiling of the rubber. No trouble in this respect is likely to arise in the boiling of very high grades of rubber, but a few of the medium and low grade brands give off an almost unbearable stench. The obvious remedy for this is to carry out the boiling in closed and ventilated vessels. The alternative of fixing a hood and ventilating shaft above the tank would, no doubt, be equally efficacious in abating the nuisance inside the workshops, but its transference to the open air in densely inhabited districts would not long be tolerated.

2. **Rubber Mixing.**—A large variety of organic and mineral compounds are mixed with india rubber, and amongst the latter the compounds of lead, zinc, and antimony occupy a very prominent place. In many rubber

factories these materials are sifted before being mixed with the india rubber, and it is still customary in many places to perform this operation by hand. It is quite needless to dwell upon the danger likely to arise from this reprehensible practice, and the sifting by machinery of all lead and zinc compounds should be rigorously insisted upon.

The mixing rollers employed in rubber factories must also be mentioned as a source of danger. These machines, as is well known, consist of two heavy rollers placed horizontally, between which the india rubber and other ingredients are worked into a homogeneous mixture. Considering the dangerous character of this kind of machine, it is really surprising that the number of accidents occurring is so small. Those that get their fingers caught somehow always manage to tear them from the grip of the rollers, though they may leave their nails behind and get their finger ends more or less severely crushed. There are, however, a number of cases on record of men not having succeeded to save themselves in this manner, but being drawn into the machine and having their arm or arms torn from their bodies. This, of course, means death in its most appalling form.

For starting and stopping, these machines possess on their driving wheels a clutch and striking gear; but it is a well-known fact, that when the machine has its load on, it is a physical impossibility to open the clutch and stop the machine. There is no reason whatever why such an inefficient type of clutch should be tolerated, as there are quite a number of clutches known which do not possess this grave defect.[1]

3. **Coal Tar Naphtha, Petroleum Spirit, Shale Oil.**—These well-known solvents are the cause of a good deal of trouble in india rubber works. In those workrooms in which these solvents are not deliberately evaporated, where, therefore, they are only exposed to normal workshop temperatures, no inconvenience is experienced, as it is obviously in the interest of the manufacturer to adopt all possible means to avoid a premature evaporation—*i.e.*, waste of solvents. The case is different in those rooms in which these solvents are purposely evaporated so as to leave a dry coat of rubber on a textile fabric. Evaporation of the solvents is carried out on the machines known as 'spreading machines,' and used in the manufacture of waterproof cloth. This industry has assumed enormous proportions. The yearly production of waterproof fabrics in Great Britain alone amounts, on a moderate computation, to at least 125,000 pieces of 60 yards each. Taking the very moderate average of 8 oz. dry weight of rubber mixing per yard of cloth, and taking the 'naphtha moisture' of the rubber doughs used as amounting to 50 per cent., also a moderate estimate, this would give us the quantity of solvents evaporated in British factories alone as amounting to 2000 tons, or say 600,000 gallons, per annum. It is therefore not to be wondered at that the atmosphere, even in the most modern

[1] A very ingenious device, enabling the worker to stop his machine practically instantly even if both his hands should be caught, has been described by Mr F. CLOUTH in his book on *Gummi, Guttapercha und Balata*, Leipzig, 1899.

and spacious of spreading rooms, is quite unbearable for anybody not inured to it, and becomes at times even unbearable to the workmen, who then resort to the simple British plan, not unknown in respect of less objectionable occupations, of 'walking out of it.'

Upon the question whether the vapours of the above named rubber solvents are dangerous to health, I do not feel competent to express an opinion. They certainly irritate the eyes and the respiratory organs, but this effect is not observable in those accustomed to work in an atmosphere charged with these vapours. On the other hand, there is no doubt whatever that working in the atmosphere of a spreading room very frequently produces strongly marked effects on the men, who often plainly show all the symptoms of intoxication. Under specially unfavourable conditions cases of actual stupor and markedly dilated pupils not infrequently occur. Even where these symptoms are absent there is generally a decided increase of the frequency of the pulse. The latter I have repeatedly observed as high as 86 per minute. In young boys who are new to the work, this naphtha intoxication produces a curious hysterical condition followed by stupor. The effect passes off after a few hours' sleep, and gradually the boys appear to become less subject to the influence of these vapours. As a curious fact, I may mention that the number of abstainers amongst india rubber spreaders appears to be singularly small—in fact, I have never met one yet.

Whether the above conditions are matters for Government interference must be left to the medical advisers of the Home Office to decide, but there can be no doubt that it is inimical to all the interests of manufacturers to have a large body of men in their factories working all the year round in a state bordering on intoxication.

The obvious remedy for this nuisance, to apply a very lenient term to it, is not to allow these solvents to pass into the atmosphere, but to condense them as soon as they are formed. This problem has attracted the attention of quite a number of manufacturers and inventors, many firms putting up installations for the purpose. Most of these were abandoned after a period of experimenting; some of them are working still, but, from all the information I could gather, with rather indifferent results. This, in my opinion, is entirely due to the wrong principles upon which the plants in question were or are constructed.

It appears that in every case the essential features of the plant employed were practically the same: a low cowl or hood is fixed over the heating chests upon which the rubber-coated fabrics are dried. By connecting this cowl through some form of condenser with a suction pump or fan, the naphtha vapours rising from the fabrics are carried through a condenser. But it will be seen that in order to lift the naphtha vapours from the cloth and to carry them to the condenser, a current or volume of air is required greatly exceeding the volume of the naphtha vapours to be condensed. This subsequently impedes considerably the efficiency of

the condenser, owing to the low heat conductivity of air; and as, moreover, the hydrocarbons in question possess a very considerable vapour tension even at ordinary temperatures, it is obvious that a considerable proportion of the vapours thus aspirated must unavoidably remain uncondensed. I am informed that the best results obtained with this description of plant varied from 20 to 25 per cent. of the quantity of naphtha carried by the rubber-coated fabrics. Against this there was the cost of the suction current and of the working of the condenser, which, together with the charges for interest on capital and depreciation, rendered the process unremunerative. To this must be added the danger arising from fires, the latter tending at once to spread from one machine to the other when they were all connected by the above named suction tubes, and the possibility of serious explosions of the mixtures of air and naphtha vapours.

To my mind all these attempts were either doomed to failure at the very outset, or could, at best, attain to very mediocre results only, owing to the application of an air current for the carrying of the vapours to a condenser; and I am of opinion that the simplest, the most natural, and, at the same time, the most efficient process will be found to consist in allowing the naphtha vapours to fall by their own gravity[1] upon a suitably arranged condenser surface. Such a plant has been devised by WEBER and FRANKENBURG (Eng. Pat., No. 16,919, 1901), and it is working in a most satisfactory manner, from 60 to 70 per cent. of the naphtha carried by the rubber-coated fabric being recovered. In case of fire there is no risk of its spreading to other machines or of causing explosions, every machine being entirely self-contained.

The above named solvents are also apt to render the atmospheres of the 'making up rooms' rather oppressive, owing to the large quantities of rubber cement used in them. A 'solutioning' machine patented by J. FRANKENBURG (Eng. Pat., No. 3568, 1899) effects a great improvement in this respect at a considerable saving of the expensive rubber cement.

4. **The Vulcanising Process.**—There is nothing in any of the various methods of vulcanising india rubber by heat (in conjunction with sulphur) which could detrimentally affect the workers. As the temperature is rather a high one, in some of the methods small quantities of sulphur vapour being given off, the rooms in which these processes are carried out should be spacious and effectually ventilated.

The 'cold' process of vulcanisation, with a solution of sulphur monochloride in carbon bisulphide, has already, on the part of the Home Office, been made the subject of a number of regulations and rules respecting the men employed. The strict administration of these regulations under the control of the factory inspectors has now almost completely stopped the

[1] It is curious to see how persistently rubber manufacturers and engineers treat the vapours of these solvents, and of carbon bisulphide, as 'light vapours,' meaning thereby lighter than air; whereas, as a matter of fact, the vapours of solvent naphtha are several times as heavy as air—*i.e.*, about as heavy as is zinc compared with water.

occurrence of acute and chronic cases of poisoning with carbon bisulphide which were formerly so common.

As regards the machinery by which this process is at present carried out, this is still capable of considerable improvement. Its present form is very primitive, and only too plainly shows that it was designed with the simple view to its purpose, but without the least regard of some of the physical peculiarities and of the dangers to life and limb likely to arise from these. Of course I do not suggest that these omissions were intentional—in fact, I am quite certain that they are simply due to the entire lack of physical and chemical knowledge on the part of those who designed them. A rationally constructed 'sincaloring' machine will not only produce superior goods, but it will also entirely prevent those disastrous explosions which have been uncomfortably numerous of recent years. It even appears to me perfectly feasible to prevent altogether the discharge, now practised, of the carbon bisulphide vapours into the open atmosphere, and to recover practically the whole of them. This would finally remove one of the last remaining of the serious objections against the use of carbon bisulphide in rubber works. The discharge of enormous quantities of the vapours of this obnoxious liquid within more or less densely inhabited districts is a piece of unmitigated barbarism.

The substitution of other solvents—benzene, petroleum spirit, carbon tetrachloride—for carbon bisulphide has been attempted times without number, but without any satisfactory result. The reason of this is, of course, that the carbon bisulphide employed in the process does not act as an indifferent solvent merely for the sulphur monochloride, but has a specific physical effect upon the india rubber, which is absent in any of the above named proposed substitutes (*see* page 199).

From the above it will be seen that the sources of danger to health peculiar to the india rubber industry are few, and, such as they are, unquestionably capable of being worked in such a manner as to preclude entirely their affecting the workpeople to any appreciable degree. This desirable state has not been realised at the present moment, or very imperfectly only, but we are gradually getting nearer to it, thanks partly to the common-sense of the manufacturers, partly to the pressure exerted in this direction by the Home Office.

THE END.

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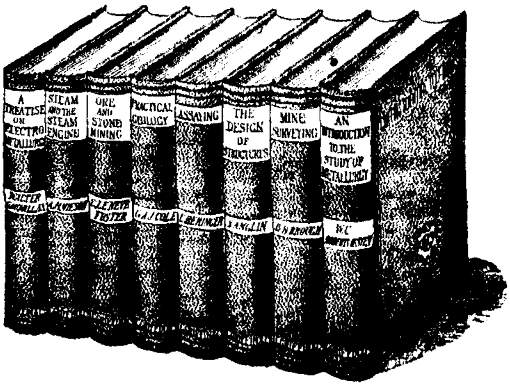

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